Synthesis and fluxional behaviour of (cyclopentadienyl) and (pentamethylcyclopentadienyl)ruthenium(II) complexes with hemilabile ether-phosphines. 31P DNMR spectroscopic studies and line shape analysis


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Synthesis and fluxional behaviour of (cyclopentadienyl) and (pentamethylcyclopentadienyl)ruthenium(II) complexes with hemilabile ether-phosphines. $^{31}$P DNMR spectroscopic studies and line shape analysis

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Abstract

A series of Cp*RuCl(P−O)$_2$ complexes (3a−e) (Cp* = η$^5$-C$_5$Me$_5$) were prepared in situ by reaction of [Cp*RuCl$_2$]$_2$ (1) with the ether-phosphine ligands Ph$_3$PCH$_2$−D (2a−d) (D = CH$_3$, OCH$_3$ (a), 1,3-dioxolane-2-yl (b), 1,3-dioxane-2-yl (c), 1,3-dioxepane-2-yl (d), tetrahydrofuran-2-yl (e)) in the presence of zinc. Treatment of 3a−e and CpRuCl(P−O)$_2$ (4b,c) with AgSbF$_6$ and Na$_2$P$_2$H$_5$, respectively, afforded ionic, monochelated ruthenium(II) complexes of the type [($η^5$-C$_5$R$_5$)Ru(P−O)(P−O)]$^+$ (5a−e. R = CH$_3$; 6b,c; R = H). The fluxional behaviour of 5a−e and 6c was studied by temperature dependent $^{31}$P NMR investigations. In the case of 5a−e computer-generated spectra were fitted to the experimental by using DNMR5. Thermodynamic parameters $\Delta H^*$, $\Delta S^*$ and $\Delta G^*$ were obtained via graphical application of the Eyring equation to the kinetic data. Stirring 5c, 6c under an atmosphere of carbon monoxide results in the formation of [(η$^5$-C$_5$R$_5$)Ru(CO)(P−O)]$^+$[SbF$_6$] (7c; R = CH$_3$, 8c; R = H).

Key words Ruthenium complexes; Cyclopentadienyl complexes, Ether-phosphate complexes

Introduction

Half-sandwich (cyclopentadienyl)ruthenium(II) systems have been reported as an excellent organometallic auxiliary in the investigation of catalytic processes [1]. In fact easy replacement of both the chloride and the phosphines in CpRuCl(PPh$_3$)$_2$ [2] has led to a variety of new metal complexes [3−5]. Recently an interesting study in our group has involved ether-phosphines (O,P) in complexes of this type [6]. The oxygen donors in the ether moiety of these ligands may be regarded as intramolecular solvent molecules forming only weak metal−oxygen bonds which may be cleaved reversibly (P−O: $η^3$-P coordinated; P−O: $η^5$-O,P coordinated) [7]. If the molecule is such that it allows the oxygen donor atoms which belong to different O,P ligands to compete for a common coordination site, fluxional behaviour can be observed [6−9]. Referring to this the first results about dynamic processes in octahedral ruthenium(II) [8] and square-pyramidal palladium(II) complexes [9] containing ether-phosphate ligands were published recently. Contributions of the various O,P ligands to the metal−oxygen bond strength were determined via $^{31}$P DNMR spectroscopic studies.

Replacement of Cp with the more basic, electron donating pentamethylcyclopentadienyl (C$_5$Me$_5$) ligand has significantly affected the chemistry of organometallic ruthenium complexes [1, 10, 11]. Recent work by Bercaw and co-workers [11] and Suzuki and co-workers [12] has provided methodologies for the syntheses of Cp*RuCl$_2$ (L = tertiary phosphine) from oligomeric [Cp*RuCl$_2$]$_n$. The different properties of Cp* versus Cp in such systems is an area of active interest [13−16].

The present paper reports the synthesis, steric and spectroscopic properties of (cyclopentadienyl) and (pentamethylcyclopentadienyl)ruthenium(II) complexes provided with a series of ether substituents. The difference in reactivity of ionic complexes 5c and 6c with carbon monoxide is indicative for the change of the rutheni...
num-oxygen bond strength by increase of electron density in the ruthenium centre via the Cp* ligand. The main attention is focused on the fluxional processes and co-workers [12]. The ether-phosphmes 2a-e [24] density in the ruthenium centre via the Cp* hgand.

Experimental

All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR data were obtained with a Bruker IFS 48 instrument. FD mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV, 60 °C), modified by AMD. Elemental analyses were performed with a Carlo Erba 1106 analyzer; Cl and F analyses were carried out according to Schöniger [17] and analyzed as described by Dirschel and Erne [18] and Brunisholz and Michot [19]. Ru was determined and analyzed as described by Dirschel and Erne [18].

Experimental

n,n-dihexylethyl ether = 1/1 and contained pure 3a-e. The main fraction was eluated with n-hexane/diethyl ether = 5/1 as eluents the first fraction contained excess 2a-e. The main fraction was eluated with n-hexane/diethyl ether = 1/1 and contained pure 3a-e. A small amount of 1 still remained on the column. The solvent of the main fraction was removed in vacuum and 3a-e were obtained as yellow powders.

Reagents

[Cp*RuCl2]n (1) was prepared as described by Suzuki and co-workers [12]. The ether-phosphines 2a-e [24] and the complexes 4b,c [6] were synthesized according to literature procedures.

General route to Cp*RuCl(P~O)2 complexes (3a-e)

To a solution of 700 mg (2.3 mmol) [Cp*RuCl2]n, (1) in 60 ml of toluene, ether-phosphate ligands 2a-e (7.0 mmol) and 800 mg (12.2 mmol) of zinc were added. After refluxing for 12 h the colour of the dark red reaction mixture had turned to bright yellow. Excess Zn and ZnCl2, respectively, were separated by filtration. After evaporation of the solvent under reduced pressure, the product was purified by column chromatography using activated silica gel in a column of 3×25 cm. With n-hexane/diethyl ether = 5/1 as eluents the first fraction contained excess 2a-e. The main fraction was eluated with n-hexane/diethyl ether = 1/1 and contained pure 3a-e. A small amount of 1 still remained on the column. The solvent of the main fraction was removed in vacuum and 3a-e were obtained as yellow powders.

Cp*RuCl(P~O)2 (3a)

3a was obtained in 50% yield, m.p. 94–96 °C (dec.).

FD-MS: m/z 761 [M+] . Anal. Calc. for C98H84Cl2O2P2Ru (760.3): C, 63.19; H, 6.50; Cl, 4.66; Ru, 13.60. Found: C, 63.47; H, 6.73; Cl, 4.70; Ru, 13.29%. IR (KBr): v(C=O) 1114 cm−1. 13C NMR (62.90 MHz, CDCl3, 22 °C): δ (ppm) 137.22–127.29 (m, C-Ph), 88.56 (s, C-η3-Cp*), 69.71 (s, CH2O), 57.82 (s, OCH2), 26.00 (m, 31P CP-MAS NMR spectra were collected on a Bruker MSL 200 multinuclear spectrometer with a wide-bore magnet (4.7 T), referenced to NH4HCO3. Magic angle spinning was performed at a 3.5 kHz spinning rate (297 K) in double-bearing rotors of ZrO2.

3P DNMR experiments were carried out on a Bruker AC 80 instrument. A 10-mm NMR tube was charged with ~30 mg of the complex and 2.4 ml of THF.

Variable temperature 31P NMR spectra were collected at 10 °C intervals in the temperature range between 181 and 325 K. Near coalescence temperatures, spectra were recorded at 2–5° intervals. The temperature was measured using a temperature control unit (VT 100 Bruker instrument) and an external thermocouple (PT 100). The NMR probe temperature was calibrated using the method of Van Geet [21] and is considered accurate to ±1 K (about 20 min was required for the temperature equilibration of the NMR sample). All exchange broadened NMR spectra were simulated using DNMRS [22] available from the Quantum Chemistry Program Exchange (QCMP 365). The analysis of the rate constant data was performed with ACTPAR [23], a non-linear least-squares program to fit the values of the desired parameters. Reported values are given with standard deviations.

Cp*RuCl(P~O)2 (3b)

3b was obtained in 60% yield, m.p. 99–101 °C (dec.).

FD-MS: m/z 817 [M+] . Anal. Calc. for C98H84Cl2O2P2Ru (816.3): C, 61.80; H, 6.05; Cl, 4.34; Ru, 12.38. Found: C, 61.81; H, 6.19; Cl, 4.57; Ru, 11.70%. IR (KBr): v(C=O) 1114 cm−1. 13C NMR (62.90 MHz, CDCl3, 22 °C): δ (ppm) 137.27–127.29 (m, C-Ph), 88.43 (s, C-η3-Cp*), 69.71 (s, CH2O), 57.82 (s, OCH2), 26.00 (m, PCH2), 9.24 (s, CH3–Cp*).

Cp*RuCl(P~O)2 (3c)

3c was obtained in 64% yield, m.p. 113–115 °C (dec.).

FD-MS: m/z 845 [M+] . Anal. Calc. for C98H84Cl2O2P2Ru (844.4): C, 62.59; H, 6.33; Cl, 4.20; Ru, 11.97. Found: C, 62.75; H, 6.60; Cl, 4.27; Ru, 11.60%. IR (KBr): v(C=O) 1127 cm−1. 13C NMR (62.90 MHz, CDCl3, 22 °C): δ (ppm) 137.28–126.92 (m, C-Ph), 101.40 (s, CH), 88.63 (s, C-η3-Cp*), 66.92, 66.43 (s, O(CH2)2O), 32.72 (m, PCH2), 25 19 (s, OCH2CH2), 9.26 (s, CH3–Cp*).
Anal. Calc. for $\text{C}_{44}\text{H}_{63}\text{F}_{6}\text{O}_{3}\text{P}_{6}\text{RuSb}$ (1044.7): C, 50.59; H, 5.11; F, 10.91; Ru, 9.67. Found: C, 50.00; H, 5.14; F, 10.54; Ru, 9.62%. IR (KBr): $\nu_{nm}(\text{C}_2\text{O})$ 1123 (P ~O), 1066 (P ~O); $\nu(\text{SbF})$ 658 cm$^{-1}$.

$[\text{Cp}^*\text{Ru}(\text{P} ~\text{O})(\text{P}^\text{O})]_2\text{[SbF}_6\text{]}$ (5d)

300 mg (0.39 mmol) $\text{AgSbF}_6$ was reacted with 134 mg (0.39 mmol) $\text{AgSbF}_6$. $\text{5c}$ was obtained in 79% yield, m.p. 166 °C (dec.). FD-MS: $m/z$ 739 [M$^-$ - $\text{SbF}_6$]. Anal. Calc. for $\text{C}_{36}\text{H}_{63}\text{F}_{6}\text{O}_{3}\text{P}_{6}\text{RuSb}$ (1156.2): C, 72.72; H, 6.71; Cl, 10.20; P, 6.97; $\text{SbF}_6$. Found: C, 72.67; H, 6.72; Cl, 10.16; P, 6.97; $\text{SbF}_6$.

Preparation of $[\text{Cp}^*\text{Ru}(\text{P} ~\text{O})(\text{P}^\text{O})]_2\text{[BF}_4\text{]}$ (5d)

To a solution of 300 mg (0.34 mmol) $\text{3d}$ in 10 ml of $\text{CH}_2\text{Cl}_2$, 118 mg (0.34 mmol) $\text{NaBF}_4$ was added. The reaction mixture was stirred overnight at ambient temperature. After removal of the solvent under vacuum, the residue was redissolved in 20 ml of dichloromethane and stirred under an atmosphere of CO. After 10 min the bright orange colour of the solution had turned completely into pale yellow. After removal of the solvent under vacuum, the residue was stirred in 10 ml of n-hexane. The pale yellow solid was...
collected by filtration (G3) and dried under vacuum. Yield 82%, m.p. 108–110 °C (dec.). FD-MS: m/z 837 [M⁺ - SbF₅]. Anal. Calc. for CₙH₉F₉O₅P₉RuSb (1072.7): C, 49.62; H, 5.00; F, 9.86; Ru, 9.39%. IR (KBr): ν(CO) 1946; ν(SbF₅) 658 cm⁻¹.

Preparation of [CpRu(P=O)₂(CO)][SbF₅] (8c)
A solution of 120 mg (0.12 mmol) of 6c in 15 ml of dichloromethane was stirred overnight under an atmosphere of carbon monoxide at ambient temperature. After this colour of the mixture has changed from bright orange to pale green. The solvent was removed under reduced pressure and the residue was stirred in 10 ml of n-hexane. The pale green solid was collected by filtration (G3) and dried under vacuum. Yield 76%, m.p. 240 °C (dec.). FD-MS: m/z 767 [M⁺ - SbF₅]. Anal. Calc. for CₙH₉F₉O₅P₉RuSb (1002.5): C, 47.92; H, 4.32; F, 11.37; Ru, 10.08. Found: C, 47.76; H, 4.42; F, 11.08; Ru, 10.34%. IR (KBr): ν(CO) 1976; ν(SbF₅) 659 cm⁻¹.

Results and discussion
Syntheses of Cp*RuCl(P=O)₂ (3a-e)
Oligomeric [Cp*RuCl₂ₐ] (1) [11, 12] has been described as an excellent precursor for the preparation of Cp*RuCl₂ complexes (L=tertiary phosphine) in the literature of the last few years [12-16]. The reduction of Ru(III) in 1 was achieved either by prolonged heating of 1 with excess phosphine in absolute ethanol [14] or by treatment of 1 with phosphine in benzene in the presence of Zn as reported by Morris and co-workers [15, 16]. Thus, very long reaction times for the generation of (pentamethylcyclopentadienyl) ruthenium(II) complexes are required following the first pathway [14]. In analogy to the second method we obtained 3a-e by reaction of the ether-phosphines 2a-e (Scheme 1) with 1 in toluene and additional Zn (Scheme 2). The chloro

[Scheme 1. Schematic representation of the employed ether-phosphine ligands 2a-e]

The ¹³C NMR spectra of 3a-d measured at 22 °C are comparable to related CpRuCl(P=O)₂ complexes [6]. In addition a singlet due to the CH₃ groups of the Cp* ring is shown in the narrow range 9.2–9.3 ppm. In the IR spectra the antisymmetric C=O vibration of the ether moiety is observed as a significant single band in the range 1105–1127 cm⁻¹. However, the ³¹P NMR spectra (Table 1) indicate the difference between Cp or bulky Cp* ligand in these systems. At −80 °C the complexes 3a-d display an AB pattern resulting from two different phosphorus atoms. When the temperature is raised the two resonances begin to broaden finally averaging to a single peak at room temperature. This phenomenon may be explained with a hindered rotation about the Ru–P bond due to the steric strain of the Cp* ligand. A similar observation was reported by Mynott et al. via ¹³C NMR spectroscopic studies investigating (cyclopentadienyl)bis(phosphine)ruthenium(II) complexes which contain π-alkene ligands [25]. The ¹³C NMR spectrum of 3a recorded at −80 °C (20.15 MHz) shows only broad signals for all carbon atoms of the ether-phosphine ligands but sharp res-
Diastereomers of Cp*RuCl(P−O), (3e)

Two diastereomer forms for complex 3e occur due to the stereogenic β carbon centre of the ether-phosphine ligand 2e. If the ruthenium is coordinated by two single resonances at 39.3 and 33.5 ppm in the 31P CP-MAS NMR spectrum of 3d. A temperature dependent 31P NMR spectroscopic study of complex 3d in toluene was carried out to determine the barrier of Ru−P rotation ΔG∞. Using DNMRS [22] and ACT-PAR [23] the obtained values are as follows: Tc = 250 K; ΔG∞ = 47.3 ± 1.4 kJ mol−1 (with the required law of propagation of errors); ΔH∞ = 38.7 ± 1.0 kJ mol−1; ΔS∞ = −34.3 ± 3.9 J mol−1 K−1.

TABLE 1 31P NMR dataa of complexes 3a−c, 5a−e, 6b,c, 7c, 8c

<table>
<thead>
<tr>
<th>Complex</th>
<th>T (°C)</th>
<th>δ (ppm)</th>
<th>3JPP (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>−80</td>
<td>34.0(d), 27.6(d)</td>
<td>42.7</td>
</tr>
<tr>
<td>3b</td>
<td>−80</td>
<td>36.0(d), 29.3(d)</td>
<td>43.6</td>
</tr>
<tr>
<td>3c</td>
<td>−80</td>
<td>38.3(d), 29.9(d)</td>
<td>42.7</td>
</tr>
<tr>
<td>3d</td>
<td>−80</td>
<td>37.9(d), 31.3(d)</td>
<td>43.4</td>
</tr>
<tr>
<td>3e</td>
<td>−80</td>
<td>38.4(d), 31.8(d)</td>
<td>43.1</td>
</tr>
<tr>
<td>5a</td>
<td>−30</td>
<td>51.2(d), 31.7(d)</td>
<td>33.8</td>
</tr>
<tr>
<td>5b</td>
<td>−54</td>
<td>59.2(d), 26.9(d)</td>
<td>32.5</td>
</tr>
<tr>
<td>5c</td>
<td>−90</td>
<td>47.3(d), 30.9(d)</td>
<td>32.2</td>
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<tr>
<td>5d</td>
<td>−63</td>
<td>43.3(brs), 32.3(d)</td>
<td>33.9</td>
</tr>
<tr>
<td>5e</td>
<td>−30</td>
<td>52.0(d), 31.4(d)</td>
<td>33.9</td>
</tr>
<tr>
<td>6b</td>
<td>−30</td>
<td>48.3(d), 35.8(d)</td>
<td>35.3</td>
</tr>
<tr>
<td>6c</td>
<td>−30</td>
<td>65.5(d), 23.6(d)</td>
<td>35.1</td>
</tr>
<tr>
<td>6c</td>
<td>−30</td>
<td>69.6(d), 30.2(d)</td>
<td>36.6</td>
</tr>
<tr>
<td>7c</td>
<td>−30</td>
<td>65.7(d), 31.7(d)</td>
<td>35.1</td>
</tr>
<tr>
<td>8c</td>
<td>−30</td>
<td>40.4(d), 30.8(d)</td>
<td>36.6</td>
</tr>
</tbody>
</table>

a32.44 MHz. bIn CH2Cl2. cIn toluene. dIn THF. eω10 = 135 Hz

Spectroscopic data of [Cp*Ru(P−O)(P−O)]2[SbF6] (5a)

The 31P NMR spectrum (Table 1) of 5a reveals an AB pattern caused by the η5−O,P chelating and η1−P coordinated ligands. A band at 1064 cm−1 in the IR spectrum is characteristic for η5−O,P chelation of one ether moiety, while the absorption at 1100 cm−1 indicates η1−P coordination of the second ligand [24].

Spectroscopic and steric properties of [(η5−C5R5)Ru(P−O)(P−O)]+ (5b−d, 6b,c)

The 31P NMR spectra of the cationic monochelated complexes [(η5−C5R5)Ru(P−O)(P−O)]+ (5b−d, 6b,c) at low temperatures show that two diastereomers may be formed caused by chirality at the ruthenium centre in addition to C chirality, resulting from η2−complexation of the O,P ligand (Table 1). Atomic models of complexes 5b−d, 6b,c suggest that the strain is stronger in the RMRSC/SMSRc diastereomer, because the cyclic ether moiety interferes with the Cp or Cp* ligand (Scheme 3). A similar observation was reported in the current literature investigating (η5−C5H5)Os complexes which contain op-
tional active amino carboxylate ligands [28]. However, the presence of the two possible diastereomeric forms is strongly dependent on the employed ether-phosphate ligand and on the \( \eta^1\)-C,R, ligand, respectively. In the complexes 6b,c containing the Cp ligand both diastereomers were obtained in an approximate 1:1 ratio (Table 1). The low and high field signals in the \(^{31}\)P NMR spectrum can be traced back to the \( \eta^2\)-O,P and \( \eta^1\)-P coordinated ligands. There is a remarkable chemical shift difference between the resonances of the respective \( \eta^2\)-O,P chelating ligands of the two diastereomers (65.5 and 48.6 ppm for 6b; 65.7 and 40.4 ppm for 6c). In the case of 5b both diastereomers can be observed in the \(^{31}\)P NMR spectrum in an approximate 9:1 ratio. The main diastereomer shows signals at 59.2 and 26.9 ppm due to \( \eta^2\)-O,P and \( \eta^1\)-P coordinated ligands, respectively (Table 1). Complexes 5c,d which contain the bulkier ether-phosphines 2c,d exhibit one AB pattern at low temperature indicating that only one diastereomer is present which is readily interpretable as the sterically favoured \( R_mS_c/S_mR_c \) form. The resonance of the \( \eta^2\)-chelating phosphorus atom in these complexes can be observed at relatively high field compared to the corresponding \( \eta^2\)-O,P coordinated phosphorus atom of the main diastereomer of 5b. Hence, due to the use of the less bulky O,P ligand 2b complex 5b obviously seems to contain the sterically stronger \( R_mR_c/S_mS_c \) form as the main product. The IR spectra of 5b–d, 6b,c show typical bands in the ranges 1066–1075 and 1105–1175 cm\(^{-1}\) which can be assigned to the antisymmetric \( \delta_{\text{C,O}} \) ether vibration of the \( \eta^2\)-O,P chelating and \( \eta^1\)-P coordinated ligand, respectively.

Spectroscopic data of diastereomeric forms of \([\text{Cp}^*\text{Ru}(\eta^2-O)(\eta^2-O)]\text{[SbF}_6\text{]} \text{ (5e)}\)

Chloride abstraction from diastereomeric \( \text{Cp}^+\text{RuCl}(\eta^2-O) \text{ (3e)} \) containing the chiral ether-phosphate ligand 2e affords cationic monochelated \([\text{Cp}^*\text{Ru}(\eta^2-O)(\eta^2-O)]\text{[SbF}_6\text{]} \text{ (5e)} \). Due to three chiral centres in this molecule four diastereomeric forms are expected. However, the \(^{31}\)P NMR spectrum of 5e demonstrates the presence of only two diastereomers (Table 1). Further classification of this system was achieved by a 2D-(P,P)-chemical shift-COSY spectrum showing an AB pattern with resonances at 52.0 and 31.4 ppm and an A'B' pattern at 48.3 and 35.8 ppm, respectively, in an approximate 2:1 ratio. Moreover, two absorptions in the IR spectrum at 1066 and 1095 cm\(^{-1}\) can be traced back to one \( \eta^2\)-O,P chelating and one \( \eta^1\)-P coordinated ligand.

Dynamic behaviour and variable-temperature \(^{31}\)P NMR studies of 5a–e, 6c

Variable-temperature \(^{31}\)P NMR spectroscopy is an excellent method investigating fluxional processes of transition-metal complexes containing monodentate (P − O) and bidentate (P'O) ether-phosphate ligands [6–9]. It is known, that the metal–oxygen bond strength and thus the fluxional behaviour depends on the employed O,P ligands caused by their oxygen basicities and steric constraints [8, 9].

A temperature dependent \(^{31}\)P NMR investigation of the salt \([\text{CpRu}(\eta^2-O)(\eta^2-O)]\text{[SbF}_6\text{]} \text{ (6c)} \) containing the weak oxygen basic and bulky O,P ligand 2c [8] was carried out in the temperature range between –50 and 50 °C. The spectra show line broadening at 10 °C, which is reversible between 10 and 50 °C. At temperatures above 50 °C complex 6c was dissolved in 1,1',2,2'-tetrachloroethane, but unfortunately decomposition of 6c took place in this solvent at high temperatures preventing the coalescence temperature to be reached. This behaviour demonstrates a very strong ruthenium–oxygen bond strength caused by the less electron rich ruthenium centre as reported for the corresponding system containing the ether-phosphine ligand 2a [6]. Referring to this, the only way to labilize the Ru–O bond strength seems to be by increasing the electron density at the ruthenium which is possible by employing a more basic, electron donating pentamethylcyclopentadienyl ligand.

The temperature-dependent \(^{31}\)P NMR spectra of \([\text{Cp}^*\text{Ru}(\eta^2-O)(\eta^2-O)]\text{[SbF}_6\text{]} \text{ (5a–e)} \) indicate that the compounds are fluxional in solution which is regarded as evidence for the decrease of the ruthenium–oxygen bond strength by replacement of Cp versus Cp* in these complexes. The spectra of 5a, 5e,d display typical AB patterns at low temperatures, whereas 5b consists of two diastereomeric forms due to C chirality of the
**TABLE 2. Coalescence temperatures and Eyring activation parameters for fluxional processes in 5a-e**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( T_c ) (K)</th>
<th>( \Delta H^{\ddagger} ) (kJ mol(^{-1}))</th>
<th>( \Delta S^{\ddagger} ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta G^{\ddagger} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>256</td>
<td>42.4 ± 1.2</td>
<td>-22.7 ± 4.4</td>
<td>48.2 ± 1.6</td>
</tr>
<tr>
<td>5c</td>
<td>275</td>
<td>43.6 ± 2.7</td>
<td>-26.4 ± 2.7</td>
<td>50.9 ± 3.8</td>
</tr>
<tr>
<td>5b(^c)</td>
<td>274</td>
<td>49.9 ± 2.7</td>
<td>6.8 ± 10.0</td>
<td>48.0 ± 3.8</td>
</tr>
<tr>
<td>5a</td>
<td>285</td>
<td>51.3 ± 1.1</td>
<td>-31.1 ± 8.8</td>
<td>52.7 ± 1.5</td>
</tr>
<tr>
<td>5e(^e)</td>
<td>320</td>
<td>52.0 ± 2.6</td>
<td>-25.0 ± 8.4</td>
<td>60.0 ± 3.8</td>
</tr>
<tr>
<td>5e(^f)</td>
<td>&gt;325(^g)</td>
<td>56.3 ± 2.2</td>
<td>-13.9 ± 7.0</td>
<td>61.0(^h)</td>
</tr>
</tbody>
</table>

*Calculated using a modified version of DNMR5 [22] and ACTPAR [23]. \(^a\)Calculated at 298 K using the required law of propagation of errors. \(^b\)Calculated at \( T_c \) using the required law of propagation of errors. \(^c\)Calculation was performed only for the main diastereomer. \(^d\)Due to A'B' pattern. \(^e\)Due to AB pattern. \(^f\)Not obtained due to the boiling point of THF. \(^g\)Calculated at 330 K (estimated \( T_c \)) using the approximate equation \( \Delta G^{\ddagger} = \Delta G^{\ddagger} \) (22.96 + ln \( T_c/\delta T \)).

\( \eta^2 \)-O,P chelated ligand. As the temperature is raised, the resonances first broaden, then coalesce (Table 2) with final averaging in sharp singlet in all cases.

In the \( ^{31}P \) DNR spectra of 5c,d consisting of only one diastereomer (see above), at low temperatures an additional dynamic phenomenon is observed. Below \(-30 \,^{\circ}C\) the doublet in the high field range due to \( \eta^2 \)-P coordinated phosphorus becomes sharp while the signal at lower field caused by the \( \eta^2 \)-O,P chelated ligand remains broad or nearly disappears in the base line. Whereas in complex 5e the broad signal is changing into a sharp doublet at \(-90 \,^{\circ}C\), it cannot be resolved in the case of 5d until \(-100 \,^{\circ}C\) (Table 1). A rotation around the C–C bond which would lead to an exchange in the coordination of the two oxygen atoms of the chelating O,P ligand would require the dissociation of the metal–oxygen bond. This has been shown to have an energy barrier which is higher (Table 2) than the exchange process responsible for the line broadening of the low field part of the AB pattern. Thus the low energy dynamics may be attributed to conformational changes of the six- and seven-membered ether rings which are coordinated to the ruthenium centre. The \( ^{31}P \) NMR spectrum of 5e shows one AB and one A'B' pattern at \(-30 \,^{\circ}C\) due to two diastereomeric forms. When the temperature is raised, the resonances of the diastereomers begin to broaden but with different rate constants \( k_1/k_2 \). At 320 K coalescence of the A'B' pattern is achieved in contrast to the AB pattern which consists of two broad signals until 325 K (Fig. 1). Due to the boiling point of THF a temperature above 325 K was not available.

The temperature data of compounds 5a-e reveal an averaging of magnetic environments on the NMR time scale at higher temperatures indicating mutual exchange of the two O,P ligands. The exchange mechanism shown in Scheme 4 involves primarily cleavage of the Ru–O bond followed by recombination of the Ru–O bond by the oxygen atom of the second ether-phosphine ligand. All phenomena are reversible.
Additional measurements of 5a–e in CH₂Cl₂ at low temperatures show similar line shapes and nearly the same chemical shifts. Hence, a strong coordination of the THF molecule to the fluxional system can be excluded.

Using DNMR5 [22], computer-generated spectra were obtained and iteratively fitted to the experimental spectra in order to evaluate the rate constants for the exchange process at different temperatures. Graphical application of the Eyring equation to the kinetic data involving a non-linear least-squares program (ACTPAR [23]) afforded the thermodynamic parameters ΔH*, ΔS*, ΔG* and ΔG*_{298} (Table 2). In all cases the entropies show small positive or negative values indicating an intramolecular exchange [8]. The difference between the ground-state and transition-state energies is reflected by ΔG*, while ΔH* may be best interpreted as an indication of the Ru–O bond strength. The calculated values of ΔH* in 5a–e exhibit that ether-phosphines 2a–e form a stronger Ru–O contact than the O,P ligands 2b–d with two oxygen donors in 1,3-position in these systems. Thus, the Ru–O bond strength in complexes 5b–d is decreased with increase of the ring size of the cyclic ether moiety because bulky O,P ligands are able to cause steric destabilization of the ground state relative to the transition state, hence reducing the barriers of fluxionality [8]. Complex 5c with the strong basic ether-phosphate ligand 2e gives two different ΔH* values due to the two diastereomeric forms.

Preparation and spectroscopic data of [(η⁵-C₅R₅)Ru–(P~O)₂(CO)]/[SbF₅] (7c, 8c)

Cleavage of the ruthenium–oxygen contact in catonic monochelated complexes [(η⁵-C₅R₅)Ru(P~O)(P=O)]-[SbF₅] (5c, 6c) takes place by reaction with strong donor–acceptor ligands, e.g. carbon monoxide. If 5c, 6c are stirred under an atmosphere of CO at ambient temperature, a colour change of the reaction mixture indicates the formation of the stable complexes [(η⁵-C₅R₅)Ru(P=O)₂(CO)]/[SbF₅] (7c, 8c) (Scheme 1). The completion of the reaction is detected by 31P NMR spectroscopy. Whereas in the case of 5c the corresponding carbon monoxide complex 7c was obtained after only 10 min, a reaction time of approximately 12 h is required for 6c (Table 1). These differences in reactivity demonstrate the increase of electron density at ruthenium and thus the decrease of the Ru–O bond strength on replacing Cp by Cp⁺. 7c and 8c show a single absorption in the IR spectrum at 1946 and 1976 cm⁻¹, respectively.

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References

22. The routines of data input and data conversion were modified by Hartwig Kubach, Universität Tübingen, Germany 1992.