

Synthesis of new (cyclopentadienyl)rutheniumphosphine complexes with hemilabile ether-phosphines. The X-ray structure of $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2$

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Abstract

The reaction of $\text{CpRuCl}(\text{PPh}_3)_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with excess ether-phosphine ligand ($\text{O,P} = \text{Ph}_2\text{PR}$, where R is ether containing alkyl chain) in toluene or n-heptane leads to the mixed complexes $\text{CpRuCl}(\text{PPh}_3)(\text{P} \sim \text{O})$ and/or the bis(ether-phosphine) complexes $\text{CpRuCl}(\text{P} \sim \text{O})_2$. A single X-ray structure determination has been carried out for $\text{CpRuCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2$ (**4a**): space group $P\bar{1}$, $a = 9.2806(6)$, $b = 11.9454(8)$, $c = 15.2216(9)$ Å, $\alpha = 84.482(9)$, $\beta = 74.592(5)$, $\gamma = 85.066(8)^\circ$, $V = 1616.1(3)$ Å³, $F(000) = 712$, $D_x = 1.42$ g cm⁻³, $Z = 2$, $R = 0.064$, $R_w = 0.075$. Treatment of **4a** with AgSbF_6 affords the salt $[\text{CpRu}(\text{P} \sim \text{O})(\text{P} \sim \text{O})][\text{SbF}_6]$ (**5a**), with one mono- ($\text{P} \sim \text{O}$) and one bidentate coordinating ($\text{P} \sim \text{O}$) ether-phosphine ligand. The fluxional behaviour of the cation of **5a** has been studied by temperature dependent $^{31}\text{P}\{\text{H}\}$ NMR investigations. Stirring **5a** under an atmosphere of carbon monoxide resulted in the formation of $[\text{CpRu}(\text{P} \sim \text{O})_2(\text{CO})][\text{SbF}_6]$ (**6a**). All complexes have been characterized by ^1H , $^{31}\text{P}\{\text{H}\}$, $^{13}\text{C}\{\text{H}\}$ NMR, IR, mass spectroscopy and elemental analysis.

Introduction

Ether-phosphines (O,P) have been employed as ligands in the case of many transition metal complexes to mimic or to create catalytic active species [1]. A typical example is the hydrocarbonylation of methanol to acetaldehyde by (ether-phosphine)cobalt complexes which proceeds under high selectivity [2, 3]. These O,P ligands are provided with tertiary phosphorus atoms, which are responsible for a close contact to the metal center and also with oxygen atoms incorporated in open-chain or cyclic ether moieties. The oxygen donors may be regarded as intramolecular solvent molecules forming only weak metal–oxygen bonds which may be cleaved reversibly. As a result of this opening and closing mechanism in ruthenium complexes of the type $\text{Cl}_2\text{Ru}(\text{CO})(\text{P} \sim \text{O})(\text{P} \sim \text{O})$ ($\text{P} \sim \text{O}$: $\eta^1\text{-P}$ coordinated; $\text{P} \sim \text{O}$: $\eta^2\text{-OP}$ coordinated) we observed fluxional behaviour, because both oxygen functions compete for a vacant coordination site [4, 5]. This dynamic behaviour is

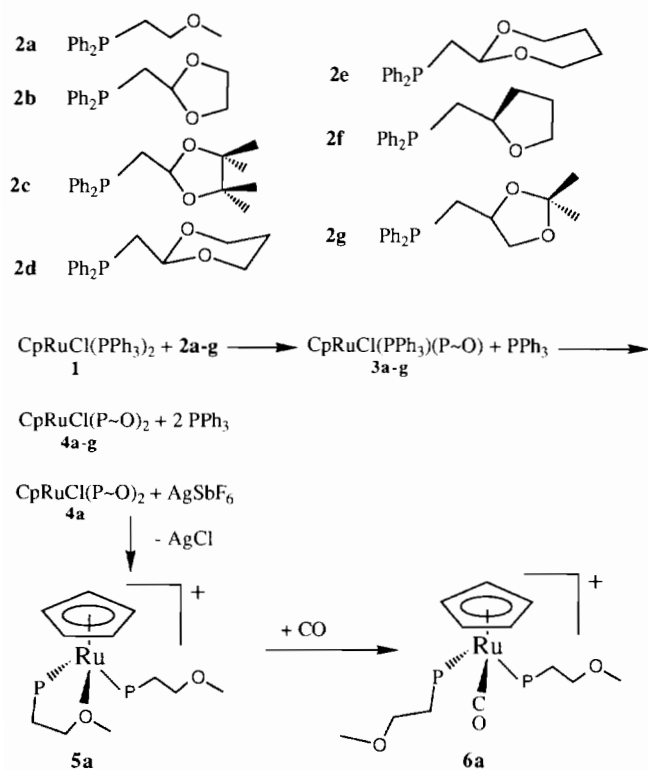
demonstrated by temperature dependent $^{31}\text{P}\{\text{H}\}$ NMR investigations.

In the last decade many complexes of the type CpRuClL_2 , with L = phosphine ligand, have been reported. The combined effects of the donor–acceptor properties of the cyclopentadienyl ligand with the electronic and steric properties of the phosphine ligands have led to a series of new metal complexes [6–8]. An interesting extension involves the use of O,P ligands in complexes of this type. Starting from $\text{CpRuCl}(\text{PPh}_3)_2$ (**1**) and the ligands **2a–g** we have prepared the neutral and ionic complexes $\text{CpRuCl}(\text{P} \sim \text{O})_2$ (**4a–g**), $[\text{CpRu}(\text{P} \sim \text{O})(\text{P} \sim \text{O})][\text{SbF}_6]$ (**5a**) and $[\text{CpRu}(\text{P} \sim \text{O})_2(\text{CO})][\text{SbF}_6]$ (**6a**), respectively, with the idea that increase of the formal charge on the metal might influence fluxional behaviour. The ligands and reactions involved are depicted in Scheme 1.

Experimental

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was obtained as a loan from Johnson Matthey, Inc. $\text{CpRuCl}(\text{PPh}_3)_2$ was prepared according

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Scheme 1. Formation of the complexes **3**, **4**, **5a** and **6a** with ligands **2a-g**.

to the literature [9]. The O,P ligands **2a-g** were synthesized following procedures described by Lindner *et al.* [10]. All syntheses were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried by refluxing over sodium. Column chromatography was performed using dried and activated silica gel (60 Mesh) as the stationary phase. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR measurements were carried out on a Bruker AMX 300 spectrometer. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Mass spectra were measured on a Varian MAT 711A spectrometer (nitrobenzylalcohol, 70 eV, 30 °C; 8 kV, 50 °C). C/H analyses were performed on an automatic microelementary apparatus model 1106 (Carlo Erba). Cl analyses were performed according to Schöniger [11]. The products were identified by elemental analysis, mass, ^1H , $^{31}\text{P}\{^1\text{H}\}$ (Table 1) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Table 2).

Syntheses of $\text{CpRuCl(P}\sim\text{O)}_2$ (**4a**, **4c-g**)

A typical method of preparation is as follows. To a solution of 230.3 mg (0.70 mmol) of ligand **2c** in 10 ml of toluene, 217.3 mg (0.30 mmol) of $\text{CpRuCl(PPh}_3)_2$ (**1**) in 20 ml of toluene were added. After refluxing for 20 h the bright yellow solution was evaporated *in vacuo* and the yellow solid washed with n-hexane (2 times 20 ml). Another portion of ligand (c. 200 mg)

was added together with 30 ml of toluene, after which the solution was refluxed for another 48 h. After evaporation of the solvent *in vacuo*, the product was purified by column chromatography (column 1×15 cm; eluents:

n-hexane/diethyl ether/dichloromethane = 20/20/1). The first colourless fraction contained PPh_3 , the second light yellow fraction excess **2c** together with a small amount of the mixed complex $\text{CpRuCl(PPh}_3)(\text{P}\sim\text{O})$ (**3c**). The third bright yellow fraction contained the pure product **4c**. Yield 220 mg (85%). **4c** was recrystallized from acetone/n-hexane.

The reaction time depends on the O,P ligand used, i.e. a total reflux time of 24–48 h (**2d**, **e**) or 72–100 h (**2a**, **c**, **f**, **g**) was employed (yields 80–90%). In the case of the chiral ligands **2f** and **2g**, the main pair of enantiomers formed in the reaction with $\text{CpRuCl(PPh}_3)_2$ could be separated by column chromatography, using an activated silica column (1×25 cm). With n-hexane/diethyl ether/dichloromethane = 20/20/1 as eluents, yellow fractions were collected in 5–7 different samples, since the diastereomers did not differ in colour. The first two samples contained the mixed complex (**3f** or **3g**), the last two samples contained the isomer in which both phosphines are either all *R* or all *S* or a mixture of those, as could be concluded from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (*vide infra*).

Synthesis of $\text{CpRuCl(P}\sim\text{O)}_2$ (**4b**)

To 409.3 mg (1.50 mmol) of ligand **2b** and 166.4 mg (0.23 mmol) of $\text{CpRuCl(PPh}_3)_2$ (**1**) were added 30 ml of n-heptane. The orange suspension turned yellow at reflux temperature. After 16 h refluxing the reaction was complete as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR. The product was separated by column chromatography (see above). Yield 149.2 mg (87%).

Syntheses of the mixed complexes

$\text{CpRuCl(PPh}_3)(\text{P}\sim\text{O})$ (**3c**, **e**, **g**)

When 1 equiv. of each O,P ligand (**2c**, **2e** or **2g**) and $\text{CpRuCl(PPh}_3)_2$ (**1**) were refluxed in 30 ml of toluene for 1 h, a mixture of complexes was formed. In addition to the starting complex **1** (10%) and the desired mixed complex **3c**, **3e** or **3g** (80%), the bis(ether-phosphine) complex **4c**, **4e** or **4g** (10%) was also obtained. The products were separated by column chromatography (eluents: n-hexane/diethyl ether/dichloromethane = 10/10/1). The first orange fraction contained **1**. The second fraction was collected in three different samples of which the first two contained the mixed complex **3c**, **3e** or **3g** in pure form. The last sample contained $\text{CpRuCl(P}\sim\text{O)}_2$ (**4c**, **4e** or **4g**).

Synthesis of $[\text{CpRu(P}\sim\text{O)}(\widehat{\text{P}}\text{O})][\text{SbF}_6]$ (**5a**)

A mixture of 100 mg (1.30 mmol) $\text{CpRuCl(P}\sim\text{O)}_2$ (**4a**) and 49.1 mg (1.43 mmol) AgSbF_6 in 15 ml of THF

TABLE 1. FD-MS, elemental analyses, $^{31}\text{P}\{^1\text{H}\}$ NMR^a and selected ^1H NMR^b data of **3c**, **e**, **g**, **4a–g**, **5a** and **6a**

Compound	FD-MS obs. (calc.)	Elemental analysis (%)			$^{31}\text{P}\{^1\text{H}\}$ NMR δ (ppm)	^1H NMR δ (ppm) Cp ^c
		C _{obs} (C _{calc})	H _{obs} (H _{calc})	Cl _{obs} (Cl _{calc})		
3c	792.2 (792.34)	(65.18)	(5.73)	(4.47)	32.38 ^d ; 43.52 ^d	4.11
3e	764.4 (764.28)	63.98 (64.43)	5.24 (5.41)	5.46 (4.64)	32.91 ^e ; 43.83 ^e	4.12
3g	764.0 (764.29)	63.78 (64.43)	4.72 (5.41)	5.71 (4.64)	34.15 ^f ; 43.90 ^f	4.12
4a	690.0 (690.17)	60.68 (60.91)	5.98 (5.70)	6.23 (5.14)	33.53 ^c	4.19
4b	746.0 (746.22)	60.61 (59.56)	5.32 (5.27)	5.50 (4.75)	32.71 ^c	4.26
4c	858.2 (858.45)	63.55 (62.96)	7.18 (6.46)	4.33 (4.13)	32.53 ^c	4.29
4d	774.3 (774.28)	61.79 (60.50)	5.05 (5.60)	5.06 (4.58)	34.42 ^c	4.23
4e	802.8 (802.34)	60.18 (61.38)	6.07 (5.91)	5.37 (4.42)	33.97 ^c	4.21
4f	742.2 (742.28)	60.93 (63.11)	5.72 (5.84)	6.04 (4.78)	36.43 ^c	4.27
4g	802.1 (802.34)	60.88 (61.38)	5.72 (5.91)	5.01 (4.42)	35.99 ^c	4.29
5a	890.4 ^g (890.49)	(47.21)	(4.42)		33.25 ^{h, i} ; 60.66 ^{h, i}	4.66 ⁱ
6a	(918.50)	(47.08)	(4.28)		34.05 ^{c, i}	5.09 ⁱ

^a22 °C, CDCl₃, 121.49 MHz. ^b22 °C, CDCl₃, 300.13 MHz. ^cSinglet. ^dd, $^2J(\text{PP}')=41.7$ Hz. ^ed, $^2J(\text{PP}')=44.2$ Hz. ^fd, $^2J(\text{PP}')=42.6$ Hz. ^gAlso $m/z=[M-\text{SbF}_6]^+$ was detected at 655.0. ^hd, $^2J(\text{PP}')=31.9$ Hz. ⁱ22 °C, CD₂Cl₂.

was stirred for 16 h at 22 °C in the dark. After evaporation of the solvent *in vacuo*, the residue was washed with diethyl ether (2 times 10 ml). The yellow solid was dissolved in 5 ml of dichloromethane and filtrated over a G4 filter to remove AgCl. The ionic complex was collected after evaporation of the solvent *in vacuo*. Yield 101 mg (80%). Because it was not possible to remove AgCl from **5a** completely, a satisfying elemental analysis could not be obtained.

Synthesis of $[\text{CpRu}(P\sim O)_2(\text{CO})][\text{SbF}_6]$ (**6a**)

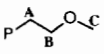
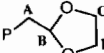
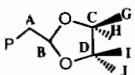
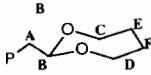
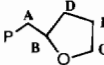
100 mg (0.11 mmol) of the ionic complex **5a** were dissolved in 10 ml of dichloromethane and stirred under an atmosphere of CO for 0.5 h. Slowly the yellow colour of the solution disappeared. After removal of the solvent *in vacuo* **6a** was obtained as an off-white solid in quantitative yield. The complex was too unstable to allow mass spectroscopy and elemental analysis. IR (cm⁻¹, CH₂Cl₂): $\nu_{\text{as}}(\text{CO})$ 1960 sst.

Structure determination and refinement of $\text{CpRuCl}(P\sim O)_2$ (**4a**)

A crystal with approximate dimensions 0.18 × 0.35 × 1.25 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-

monochromated Cu K α radiation ($\lambda(\text{Cu K}\alpha)=1.5418$ Å; $\mu(\text{Cu K}\alpha)=59.75$ cm⁻¹) and θ - 2θ scan. A total of 5457 unique reflections was measured within the range $-10 \leq h \leq 0$, $-14 \leq k \leq 13$, $-17 \leq l \leq 17$; 5239 of these were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ was 0.59 Å⁻¹. Two reference reflections ($2\bar{2}\bar{2}, 1\bar{2}\bar{2}$) were measured hourly and showed no significant decrease during the 62 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 84^\circ$. Corrections for Lorentz and polarization effects were applied. The positions of Ru, Cl and P were found by direct methods. The remainder of the non-hydrogen atoms was found in a subsequent DF synthesis. The hydrogen atoms were calculated. Block-diagonal least-squares refinement on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R=0.064$, $R_w=0.075$, $(\Delta/\sigma)_{\text{max}}=1.00$. A weighting scheme $w=(6.4+F_{\text{obs}}+0.0045F_{\text{obs}}^2)^{-1}$ was used. An empirical absorption collection (DIFABS [12]) was applied, with coefficients in the range of 0.60–1.49. A final difference Fourier map revealed a residual electron density between -1.1

TABLE 2. Selected $^{13}\text{C}\{^1\text{H}\}$ NMR data^a (δ ppm) of complexes **3c**, **e**, **4a–g**, **5a**, **6a**

Compound		Cp ^b	A ^c	B ^b	C ^b	D ^b	E ^b	F ^b	G ^b /H ^b /I ^b /J ^b
	4a	81.22	26.80	69.37	58.85				
	5a	78.82	33.31	69.50	60.42				
	6a	90.40	30.33 ^d	66.66 ^d	60.03 ^d				
	4b	81.20	31.45	103.15	64.77	65.09			
	3c	81.50	27.76	99.32	81.43	82.44			25.55, 22.57
	4c	81.44	31.80	99.55	81.74	82.71			24.09, 21.99
	4d	81.37	33.12	101.37	67.38	67.17	25.96		
	3e	81.47	27.58	100.34	65.75	65.42	29.73	29.58	
	4e	81.31	32.33	100.68	66.55	66.20	29.80	29.66	
	4f	81.10	31.25	76.77	67.83	33.50	26.02		
	4g	81.36	30.01	73.84	109.06	70.89			27.32, 26.26

^a22 °C, CDCl₃, 75.46 MHz. ^bSinglet. ^cMultiplet. ^d $\eta^2\text{-OP}$.

and 1.1 e Å⁻³ [13]. The anomalous scattering of Ru, Cl and P was taken into account. All calculations were performed with XTAL [14]. Fractional coordinates have been collected in Table 3.

Results and discussion

Syntheses of CpRuCl(P~O)₂ (**4a–g**) and CpRuCl(PPh₃)(P~O) (**3c**, **e**, **g**)

The complexes **4a–g** are obtained by reaction of excess ether-phosphine **2a–g** with CpRuCl(PPh₃)₂ (**1**) in toluene. Heating excess of O,P ligand **2a–g** with CpRuCl(PPh₃)₂ (**1**) in decaline for only 1–2 min as described by Ashby *et al.* [15] only gave the desired complex in very small yield. In the cases of ligands **2c**, **e**, **g** the product is contaminated with a small amount of the mixed complex CpRuCl(PPh₃)(P~O) (**3c**, **e**, **g**), even after prolonged heating. With less ether-phosphine or with shorter refluxing times the mixed complex can be obtained in higher yields. However, it was not possible to isolate the mixed complex in pure form by refluxing one equivalent ether-phosphine with CpRuCl(PPh₃)₂ in benzene for one hour, as reported for other phosphine ligands by Joslin *et al.* [8]. In the case of the ether-phosphines synthesized by Lindner *et al.* [10], the product was always contaminated with the bis(ether-phos-

phine) complex **4c**, **e**, **g** and starting complex **1**. Complexes **3** and **4** show two doublets and one singlet in the ³¹P{¹H} NMR spectra, resulting from two different and two equivalent phosphines, respectively (Table 1). The cyclopentadienyl protons show a singlet in ¹H NMR for all complexes (Table 1).

X-ray structure determination of **4a**

The complex CpRuCl(Ph₂PCH₂CH₂OCH₃)₂ (**4a**) has been structurally characterized by single-crystal X-ray determination. The molecule has a piano-stool structure that consists of a chlorine, a η^5 -cyclopentadienyl ring and two ether-phosphine ligands bonded to ruthenium through the phosphorus atoms. Figure 1 shows the PLUTO drawing [16]. Table 4 summarizes the selected bond distances and angles, respectively.

The Ru–Cl distance is comparable with those in other structurally characterized CpRuCl(PR₃)(PR'₃) complexes [8, 17]. The Ru–P distances of 2.306(2) and 2.314(2) Å are shorter than in CpRuCl(PPh₃)₂ (2.337(1) and 2.335(1) Å) and longer than in CpRuCl[P(CH₃)₃]₂ (mean distance 2.27(5) Å) [17]. Because the Ru–Cl and Ru–Cp bond lengths do not differ much in these complexes, the shortening of the Ru–P bond is probably not due to the electronic properties of the phosphines. It reflects most likely the lessening of the steric constraint around the ruthenium center in

TABLE 3. Fractional coordinates of the non-hydrogen atoms and equivalent isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ru	0.05806(6)	0.72463(5)	0.25330(4)	0.0530(3)
Cl	0.0904(3)	0.9275(2)	0.2168(1)	0.070(1)
P(1)	0.2164(2)	0.7212(2)	0.3475(1)	0.051(1)
P(2)	0.2381(2)	0.6709(2)	0.1248(1)	0.051(1)
C(1)	0.3584(9)	0.8292(6)	0.3210(5)	0.062(5)
C(2)	0.415(1)	0.8570(7)	0.4020(6)	0.075(6)
C(3)	0.510(2)	1.036(1)	0.363(1)	0.22(2)
C(4)	0.4410(8)	0.6905(6)	0.1056(5)	0.056(4)
C(5)	0.4749(8)	0.8129(6)	0.0807(5)	0.060(5)
C(6)	0.657(1)	0.9369(8)	0.0745(8)	0.109(9)
C(11)	0.3194(8)	0.5864(6)	0.3640(5)	0.052(4)
C(12)	0.4773(9)	0.5776(6)	0.3484(6)	0.062(5)
C(13)	0.5482(9)	0.4726(7)	0.3586(7)	0.078(6)
C(14)	0.317(1)	0.3853(6)	0.4046(5)	0.067(5)
C(15)	0.473(1)	0.3783(7)	0.3884(6)	0.072(5)
C(16)	0.2450(8)	0.4910(6)	0.3923(5)	0.059(5)
C(21)	0.1146(9)	0.7495(6)	0.4656(5)	0.059(4)
C(22)	0.148(1)	0.6916(7)	0.5425(5)	0.070(5)
C(23)	0.076(1)	0.7259(8)	0.6290(6)	0.081(6)
C(24)	-0.023(1)	0.8190(7)	0.6391(6)	0.077(6)
C(25)	-0.056(1)	0.8735(7)	0.5645(6)	0.076(6)
C(26)	0.0086(9)	0.8409(6)	0.4780(5)	0.061(5)
C(31)	0.2438(8)	0.5188(6)	0.1156(5)	0.054(4)
C(32)	0.3212(9)	0.4452(6)	0.1632(5)	0.058(4)
C(33)	0.312(1)	0.3283(7)	0.1657(6)	0.070(5)
C(34)	0.222(1)	0.2867(7)	0.1170(6)	0.074(6)
C(35)	0.149(1)	0.3568(8)	0.0682(7)	0.082(6)
C(36)	0.156(1)	0.4746(7)	0.0661(6)	0.074(6)
C(41)	0.2088(9)	0.7284(6)	0.0141(5)	0.056(4)
C(42)	0.2948(9)	0.6920(7)	-0.0672(5)	0.069(5)
C(43)	0.274(1)	0.7381(8)	-0.1495(6)	0.081(6)
C(44)	0.167(1)	0.8266(8)	-0.1518(6)	0.076(6)
C(45)	0.0807(9)	0.8662(6)	-0.0717(5)	0.063(5)
C(46)	0.1000(9)	0.8194(6)	0.0114(5)	0.059(5)
C(51)	-0.1053(9)	0.6254(8)	0.3558(5)	0.073(5)
C(52)	-0.1757(9)	0.7321(9)	0.3448(6)	0.082(6)
C(53)	-0.182(1)	0.7474(9)	0.2496(7)	0.096(7)
C(54)	-0.119(1)	0.649(1)	0.2064(6)	0.098(8)
C(55)	-0.066(1)	0.5711(8)	0.2736(7)	0.084(6)
O(1)	0.5420(8)	0.9255(7)	0.3702(6)	0.134(7)
O(2)	0.6166(6)	0.8260(5)	0.0992(4)	0.075(4)

CpRuCl(PR₃)₂ when going from PPh₃ via PPh₂(CH₂CH₂OCH₃) to P(CH₃)₃. The interatomic distances in the free ether arm correspond well with the distances reported for the monodentate coordinated Ph₂PCH₂CH₂OCH₃ in RuCl₂(CO)(P~O)(P̄O), being 1.53(2), 1.41(8) and 1.43(2) Å for C(1)–C(2), C(2)–O(1) and C(3)–O(1), respectively (the longer O–CH₃ bond length in the latter complex is artificial, since it is caused by scattering phenomena) [5].

Diastereomers of CpRuCl(P~O)₂ (**4f**, **4g**)

If the chiral ether-phosphine **2f** or **2g** is used three diastereomers are possible for the complexes CpRuCl(P~O)₂ (**4f**, **4g**), resulting from the chirality on the β carbon atom of the phosphine. If the ruthenium

is coordinated by one *R* and one *S* phosphine ligand, two mesomer forms of the complex are possible. The complex in which two *R* phosphines are coordinated is the enantiomer form of the complex with two *S* phosphine ligands (Scheme 2). This pair of enantiomers has been isolated for complexes **4f** and **4g**. The complexes **4f** and **4g** show both a singlet in the ³¹P{¹H} NMR spectrum at 36.43 and 35.99 ppm, respectively.

Ionic complex [CpRu(P~O)(P̄O)][SbF₆] (**5a**)

With weakly coordinating ligands it should be possible to bind the oxygen atom of the ether arm of one ether-phosphine ligand to the ruthenium center. This can be effected by replacing Cl⁻ by SbF₆⁻ (Scheme 1). Indeed it has been found that complex **5a** contains

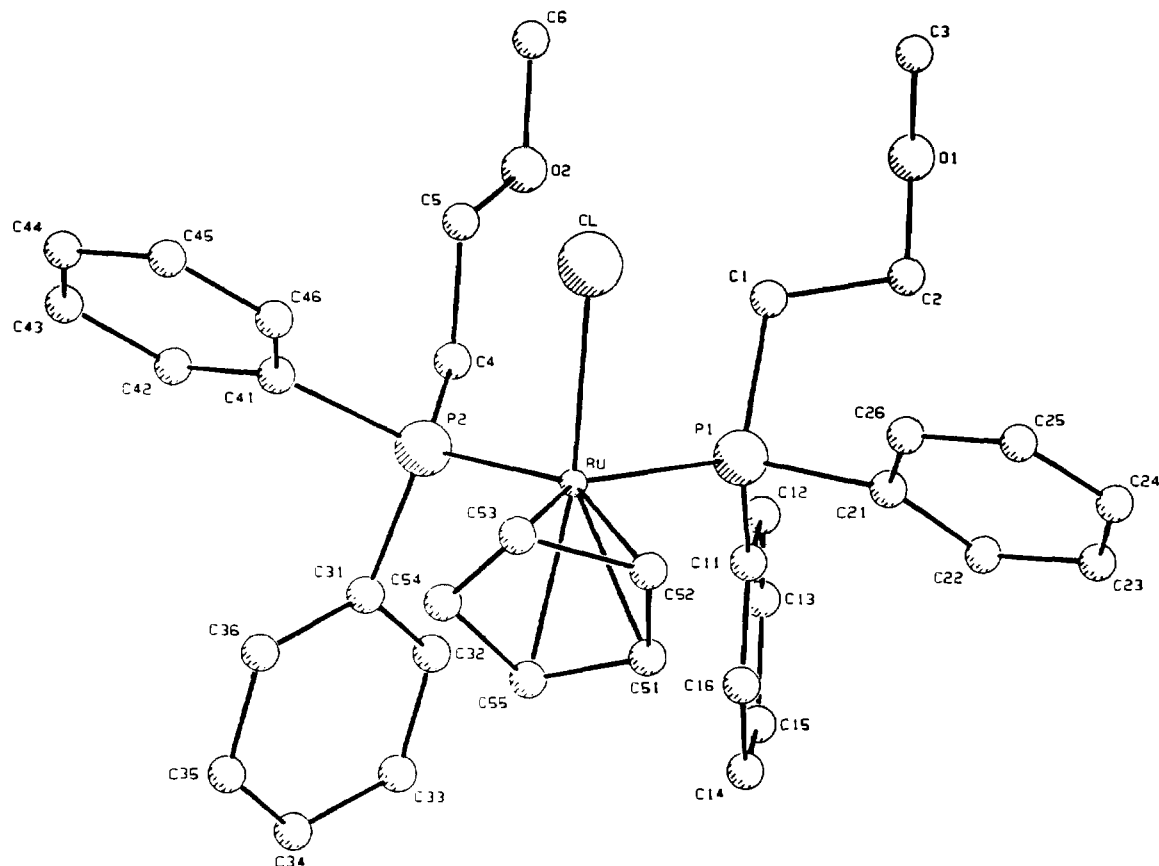
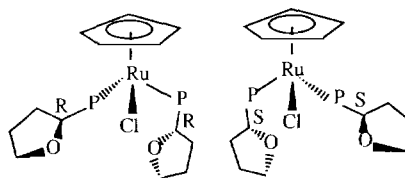


Fig. 1. PLUTO drawing of $\text{CpRuCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2$ (**4a**).

TABLE 4. Selected bond distances and angles of $\text{CpRuCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2$ (**4a**) with e.s.d.s in parentheses

Bond distances (Å)			
Ru-Cl	2.459(2)	P(2)-C(4)	1.859(8)
Ru-P(1)	2.306(2)	P(2)-C(31)	1.831(8)
Ru-P(2)	2.314(2)	P(2)-C(41)	1.836(8)
Ru-C(51)	2.199(8)	C(1)-C(2)	1.53(1)
Ru-C(52)	2.245(8)	C(2)-O(1)	1.44(1)
Ru-C(53)	2.24(1)	C(3)-O(1)	1.33(2)
Ru-C(54)	2.24(1)	C(4)-C(5)	1.51(1)
Ru-C(55)	2.20(1)	C(5)-O(2)	1.44(1)
P(1)-C(1)	1.864(8)	C(6)-O(2)	1.40(1)
P(1)-C(11)	1.832(7)		
P(1)-C(21)	1.843(7)		
Bond angles (°)			
Cl-Ru-P(1)	89.14(8)	Ru-P(2)-C(4)	123.3(3)
Cl-Ru-P(2)	94.64(7)	Ru-P(2)-C(31)	111.1(2)
P(1)-Ru-P(2)	96.67(7)	Ru-P(2)-C(41)	116.3(2)
Ru-P(1)-C(1)	117.5(3)	P(2)-C(4)-C(5)	111.3(5)
Ru-P(1)-C(11)	116.1(3)	C(4)-C(5)-O(2)	106.8(6)
Ru-P(1)-C(21)	112.1(3)	C(2)-O(1)-C(3)	116(1)
P(1)-C(1)-C(2)	115.5(5)	C(5)-O(2)-C(6)	109.8(7)
C(1)-C(2)-O(10)	110.2(7)		

one $\eta^2\text{-P}\hat{\text{O}}$ chelating ligand and one monodentate $\eta^1\text{-P}$ coordinated ligand ($\text{P}\sim\text{O}$), as indicated by $^{31}\text{P}\{^1\text{H}\}$ (Table 1) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Table 2). The lower and higher field signals in both spectra can

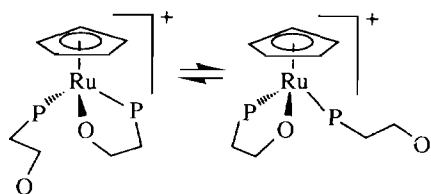


Scheme 2. The two enantiomers for $\text{CpRuCl}(\text{P}\sim\text{O})_2$ (**4f**), forming the main diastereomer (phenyl groups at phosphorus have been omitted for clarity).

be traced back to the $\eta^2\text{-}\hat{\text{O}}\text{P}$ and $\eta^1\text{-P}$ coordinated ligands, respectively.

For other ruthenium(II) complexes containing two O,P ligands of which only one coordinates via the ether arm, fluxional behaviour has been observed [4, 5, 18]. The competition of the two ether arms for one open site at the ruthenium center is observed in temperature dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra [1]. Scheme 3 shows this competition for **5a**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the ionic complex **5a** were measured between -30 and 80 °C. Complex **5a** shows line broadening at 30 °C, which is reversible between 30 and 50 °C. At temperatures higher than 50 °C decomposition of the complex unfortunately prevents the coalescence temperature to be reached. In the neutral complexes $\text{Ru}(\text{CO})\text{Cl}_2(\text{P}\sim\text{O})(\hat{\text{P}}\hat{\text{O}})$ co-



Scheme 3. Opening and closing of the ether arm.

alescence temperatures were found between 0 and 80 °C for different ether-phosphines [1]. The fact that the coalescence temperature in the case of **5a** cannot be attained indicates that the hard oxygen donor binds more strongly to the harder acid [ruthenium(II)]⁺ than to the neutral [ruthenium(II)] center in similar complexes.

Results obtained so far indicate that the fluxional behaviour of salts of type [CpRu(P~O)(P̂O)][SbF₆] strongly depends on the ether-phosphine used. Further experiments will be carried out to examine the chelating properties of the different O,P ligands in similar ionic complexes. The parameters which influence the strength of the ruthenium–oxygen bond and thus the fluxional behaviour, such as oxygen basicity, steric constraint and conformational distortions, are currently under investigation for several different ether-phosphine ligands.

Formation of [CpRu(P~O)₂(CO)]SbF₆ (**6a**)

The ruthenium–oxygen contact in [CpRu(P̂O)-(P~O)][SbF₆] (**5a**) is cleaved if **5a** is stirred under an atmosphere of CO, leading to [CpRu(P~O)₂(CO)][SbF₆] (**6a**) (Scheme 1). A singlet in the ³¹P{¹H} NMR spectrum and one CO absorption in the IR spectrum of **6a** indicate the coordination of CO. For comparison it should be noted that for [CpRu(PPh₃)₂(CO)][BPh₄], one CO absorption at 1980 cm⁻¹ (CHCl₃) was also observed [19].

The CO ligand appears to be strongly bound since irradiation at both 22 °C and reflux temperature with and without using a nitrogen stream in both CH₂Cl₂ and THF did not rupture the metal–CO bond. In similar neutral ruthenium(II) complexes, i.e. RuCl₂(CO)₂(P~O)₂ [5], CO was reversibly coordinated.

Supplementary material

Further details of the crystal structure determination are available from the authors on request.

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