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Synthesis, Structure, and Fluxional Behavior of Octahedral Ruthenium(II) Complexes with Mixed Oxygen–Phosphine Ligands. ^{31}P DNMR Spectroscopic Studies, Line Shape Analysis, and Determination of Rearrangement Barriers

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The synthesis and spectroscopic properties of ether–phosphine ruthenium(II) complexes of the type $Cl_2Ru(P\frown O)_2$ (**5a, 7a–10a**) and *trans*-$Cl_2Ru(CO)(P{\sim}O)(P\frown O)$ (**5b, 7b–10b**) are reported. Temperature-dependent ^{31}P NMR spectra of the fluxional complexes **1b–11b** and *cis*-$Cl_2Ru(CO)(P{\sim}O)(P\frown O)$ (**1c–3c**) were measured and by using a modified version of DNMR5, computer-generated spectra were obtained and fitted to the experimental spectra. Graphic application of the Eyring equation to the kinetic data afforded the thermodynamic parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$. Complex **11b** with the strong basic four-membered ether–phosphine **11** crystallizes in the monoclinic space group $P2_1/n$, with $a = 11.974(2)$ Å, $b = 10.877(2)$ Å, $c = 29.567(6)$ Å, $\beta = 96.34(3)°$, $Z = 4$, and $V = 3827.2(12)$ Å^3 ($R = 0.075$ and $R_w = 0.076$).

Introduction

Although dynamic behavior of transition metal complexes containing monodentate and bidentate ligands has been often investigated in the last few years, it remains an area of active research interest.[1-14] Most work has involved thioethers,[4] dithioethanes,[8,9] and heterobidentate ligands provided with one sulfur donor atom.[3-6] Dynamic nuclear magnetic resonance studies of sulfur inversion in platinum(II) and palladium(II) complexes[3,5] and metal-pivot processes in platinum(IV) complexes[9-11] attract much attention. Only a few reports have appeared concerning dynamic behavior in transition metal complexes with mixed hybrid oxygen–phosphine ligands.[12-17]

We are interested in fluxional processes of ruthenium(II) complexes containing monodentate (P$\sim$O) and bidentate (P$\frown$O) ether–phosphines because of their potential use as intramolecular solvent molecules in catalytic processes. These ligands form a close metal–phosphorus contact and only weaker metal–oxygen bonds which may be cleaved reversibly. In these complexes the oxygen atom is incorporated in open-chained or cyclic ether moieties. The strength of the ruthenium–oxygen bond depends on O nucleophilicity, the ring size of the cyclic ether, the number and position of the O atoms in the ring, the s-character of the lone-pairs of the oxygen atoms, and an effect due to a change of conformation upon η^2-O$\frown$P chelation of the ether-phosphine to the central atom.[18]

The present paper reports the synthesis, spectroscopic properties, and fluxional behavior of ether–phosphine ruthenium(II) complexes provided with four- to eight-membered ether substituents. Moreover the activation parameters of these compounds are compared, and two different mechanisms of exchange are discussed.

Experimental Section

All manipulations were performed by using standard Schlenk techniques under argon. Solvents were dried and stored under argon. Pentane, hexane, and diethyl ether were distilled from sodium/benzophenone. IR and far-IR data were obtained with Bruker IFS 48 FT-IR and Bruker IFS 114c spectrometers, respectively. 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 Ru were determined according to the literature.[19] ^{31}P and ^{13}C NMR spectra were recorded on a Bruker WP 80, AC 80, AC 250, or AMX 300 or a Cryospec WM 400. Chemical shifts (δ) are reported in ppm downfield from external H_3PO_4 (85% in D_2O, 1% in acetone-d_6) and Me_4Si, respectively.

^{31}P DNMR experiments were carried out on a Bruker AC 80. DNMR samples were prepared (typically 15–20 mg) under an atmosphere of argon in 10-mm NMR tubes. The complexes were dissolved in 2.4 mL of $CHCl_3$ (for temperatures <328 K) or 1,1′,2,2′-tetrachloroethane (for temperatures >328 K). Variable-temperature ^{31}P NMR spectra were collected at 10 °C intervals in a temperature range between 203 and 373 K. Near coalescence temperatures, spectra were acquired 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

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van Geet[20] 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 a modified version of DNMR5[21] available from the Quantum Chemistry Program Exchange (QCMP 365). The analysis of the rate constant data was performed with ACTPAR,[22] a nonlinear least-squares program to fit the values of the desired parameters. Reported values are given with standard deviations.

Reagents. $RuCl_3\cdot 3H_2O$ was a gift of Degussa AG. The ether-phosphine ligands **1–10**,[18] **11**,[23] and the complexes **1a–c–3a–c**,[13] **4a,b**,[24] **6a,b**,[25] and **11a,b**[23] were prepared as previously described. New compounds **5a,b**, **7a,b–10a,b**, **8d**, and **11e** have been synthesized analogously.[13,26]

Bis(chelate)ruthenium(II) Complexes $Cl_2Ru(P\frown O)_2$ (1a–11a). A 2.00-mmol sample of O,P ligands **1–11** were dissolved in dichloromethane (10 mL) and added with stirring to a solution of $Cl_2Ru(PPh_3)_3$ (959.0 mg, 1.00 mmol) in dichloromethane (20 mL). After the mixture was stirred for 30 min at room temperature, the solvent was removed under reduced pressure and the product extracted with *n*-hexane. Complexes **1a–11a** were isolated as red crystals by filtration and washed with *n*-hexane (3 × 10 mL), before drying in vacuo.

***trans*-Dichloro-*cis*-bis[(1,3-dioxane-4-ylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (5a).** **5a** was obtained as a red powder, mp 180–182 °C, in 85% yield. FD-MS: m/z 744 [M^+]. Anal. Calcd for $C_{34}H_{38}Cl_2O_4P_2Ru$: C, 54.84; H, 5.11; Cl, 9.53; Ru, 13.59. Found: C, 55.17; H, 5.23; Cl, 9.26; Ru, 13.94. IR (KBr): $\nu_{as}(C_2O)$ 1095 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 322 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 59.2 s. ^{13}C NMR (75.46 MHz, CD_2Cl_2, 22 °C): δ 140.05–129.47 (m, C-Ph), 100.18 (s, OCH_2O), 81.16 (s, CH), 68.87 (s, CH_2CH_2O), 34.20 (s, $CHCH_2CH_2$), 38.77 (m,[27] PCH_2).

***trans*-Dichloro-*cis*-bis[(1,3-dioxolane-4-ylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (7a).** **7a** was obtained as a dark red powder, mp 177–180 °C, in 79% yield. FD-MS: m/z 716 [M^+]. Anal. Calcd for $C_{32}H_{34}Cl_2O_4P_2Ru$: C, 53.63; H, 4.75; Cl, 9.90; Ru, 14.12. Found: C, 53.13; H, 5.27; Cl, 9.87; Ru, 14.24. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 324 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 63.4 s, 62.2 s.

***trans*-Dichloro-*cis*-bis[(1,3-dioxolane-2-ylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (8a).** **8a** was obtained as a dark red powder, mp 157–159 °C, in 75% yield. FD-MS: m/z 716 [M^+]. Anal. Calcd for $C_{32}H_{34}Cl_2O_4P_2Ru$: C, 53.63; H, 4.74; Cl, 9.90; Ru, 14.11. Found: C, 53.30; H, 4.75; Cl, 9.98; Ru, 13.70. IR (KBr): $\nu_{as}(C_2O)$ 1105 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 328 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2): δ 57.7 s (30 °C); 58.4 s, 56.0 s (−30 °C). ^{13}C NMR (20.15 MHz, CD_2Cl_2, 22 °C): δ 136.54–127.26 (m, C-Ph), 106.34 (s, CH), 66.22 [s, $O(CH_2)_2O$], 35.94 (m,[27] PCH_2).

***trans*-Dichloro-*cis*-bis[(1,3-dioxepane-2-ylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (9a).** **9a** was obtained as a pink powder, mp 204–205 °C, in 87% yield. FD-MS: m/z 772 [M^+]. Anal. Calcd for $C_{36}H_{42}Cl_2O_4P_2Ru$: C, 55.96; H, 5.44; Cl, 9.18; Ru, 13.09. Found: C, 54.49; H, 5.32; Cl, 9.52; Ru, 14.04. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 324 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2): δ 52.1 s (30 °C); 52.6 s, 51.6 s (−30 °C). ^{13}C NMR (75.46 MHz, CD_2Cl_2, 22 °C): δ 134.51–127.93 (m, C-Ph), 105.33 (s, CH), 71.75 (s,[28] Ru–OCH_2), 67.60 (s,[28] OCH_2CH_2), 36.71 (m,[27] PCH_2), 29.89 (s, $OCH_2(CH_2)_2CH_2O$).

***trans*-Dichloro-*cis*-bis[(1,3-dioxoctane-2-ylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (10a).** **10a** was obtained as a pink powder, mp 174–176 °C, in 82% yield. FD-MS: m/z 800 [M^+]. Anal. Calcd for $C_{38}H_{46}Cl_2O_4P_2Ru$: C, 57.00; H, 5.75; Cl, 8.86; Ru, 12.63. Found: C, 56.39; H, 5.44; Cl, 8.73; Ru, 11.76. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 332 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 49.5 s. ^{13}C NMR (62.89 MHz, CD_2Cl_2, 22 °C): δ 134.03–127.61 (m, C-Ph), 104.40 (s, CH), 69.15 (m, Ru–OCH_2, OCH_2CH_2), 35.36 (m,[27] PCH_2), 29.54 (s, $OCH_2CH_2CH_2CH_2CH_2CH_2O$), 24.71 (s, $O(CH_2)_2CH_2(CH_2)_2O$).

***all-trans*-Dicarbonylruthenium(II) Complexes $Cl_2Ru(CO)_2(P\sim O)_2$ (1d–10d)**: Carbon monoxide was bubbled through a solution of 0.50 mmol of $Cl_2Ru(P\frown O)_2$ (**1a-10a**) in dichloromethane (15 mL) at room temperature, until the initial red solution had turned to light yellow. The complexes *all-trans*-$Cl_2Ru(CO)_2(P\sim O)_2$ (**5, 7, 9, 10d**) were prepared only in solution. The compound **8d** was isolated as described as follows. The solvent was evaporated to low volume in vacuo. Then *n*-hexane was added with stirring, until the yellow product has precipitated. The solid was filtered off, washed with *n*-hexane (3 × 10 mL), and then dried in vacuo.

***trans*-Dicarbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxolane-2-ylmethyl)diphenylphospbine-*P*]ruthenium(II) (8d).** **8d** was obtained as a pale yellow powder, mp 163–165 °C, in 65% yield. FD-MS: m/z 744 [$M - CO$]$^+$. Anal. Calcd for $C_{34}H_{34}Cl_2O_6P_2Ru$: C, 52.86; H, 4.43; Cl, 9.17; Ru, 13.08. Found: C, 53.40; H, 4.22; Cl, 8.87; Ru, 13.75. IR (CH_2Cl_2): $\nu(CO)$ 2015 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 332 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 12.0 s.

Carbonylruthenium(II) Complexes *trans*-$Cl_2Ru(CO)(P\sim O)(P\frown O)$ (1b–10b). A red solution of 0.50 mmol of $Cl_2Ru(P\frown O)_2$ (**1a–10a**) in dichloromethane (15 mL) was added dropwise to a yellow solution of 0.50 mmol of *all-trans*-$Cl_2Ru(CO)_2(P\sim O)_2$ (**1d–11d**) in dichloromethane (15 mL). After the mixture was stirred at room temperature for 30 min, the solvent was removed under reduced pressure to low volume. Addition of *n*-hexane precipitated the product as an orange powder. The solid was washed with *n*-hexane and then dried in vacuo.

Carbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxane-4-ylmethyl)diphenylphosphine-*P;O′,P′*]ruthenium(II) (5b). **5b** was obtained as a pale yellow powder, mp 158–161 °C, in 68% yield. FD-MS: m/z 772 [M^+]. Anal. Calcd for $C_{35}H_{38}Cl_2O_5P_2Ru$: C, 54.46; H, 4.96; Cl, 9.18; Ru, 13.09. Found: C, 53.91; H, 5.05; Cl, 9.13; Ru, 13.48. IR (KBr): $\nu(CO)$ 1940 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 332 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −80 °C): δ 38.0 (d, $^2J_{PP}$ = 335 Hz, $P\frown O$), 15.9 (d, $^2J_{PP}$ = 335 Hz, $P\sim O$).

Carbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxolane-4-ylmethyl)diphenylphosphine-*P;O′,P′*]ruthenium(II) (7b). **7b** was obtained as a yellow powder, mp 169–172 °C, in 72% yield. FD-MS: m/z 744 [M^+]. Anal. Calcd for $C_{33}H_{34}Cl_2O_5P_2Ru$: C, 53.23; H, 4.60; Cl, 9.52; Ru, 13.57. Found: C, 53.11; H, 4.78; Cl, 10.03; Ru, 13.35. IR (KBr): $\nu(CO)$ 1933 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 338 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 42.5, 42.1 (d, $^2J_{PP}$ = 341 Hz, $P\frown O$), 19.7, 17.2 (d, $^2J_{PP}$ = 341 Hz, $P\sim O$).

Carbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxolane-2-ylmethyl)diphenylphosphine-*P;O′,P′*]ruthenium(II) (8b). **8b** was obtained as a yellow powder, mp 203–206 °C, in 52% yield. FD-MS: m/z 744 [M^+]. Anal. Calcd for $C_{33}H_{34}Cl_2O_5P_2Ru$: C, 53.27; H, 4.57; Cl, 9.53; Ru, 13.58. Found: C, 53.81; H, 4.35; Cl, 8.90; Ru, 13.11. IR (KBr): $\nu(CO)$ 1938 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 334 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 34.5 (d, $^2J_{PP}$ = 341 Hz, $P\frown O$), 17.0 (d, $^2J_{PP}$ = 341 Hz, $P\sim O$). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 22 °C): δ 204.61 (m, RuCO), 133.92–127.64 (m, C-Ph), 106.46 (s, CH), 64.93 [s, $O(CH_2)_2O$], 30.93 (m,[27] PCH_2).

Carbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxepane-2-ylmethyl)diphenylphosphine-*P;O′,P′*]ruthenium(II) (9b). **9b** was obtained as a pale yellow powder (the solution is very air-sensitive!), mp 160–162 °C, in 42% yield. FD-MS: m/z 801 [M^+]. Anal. Calcd for $C_{37}H_{42}Cl_2O_5P_2Ru$: C, 55.50; H, 5.28; Cl, 8.85; Ru, 12.62. Found: C, 56.33; H, 5.80; Cl, 8.73; Ru, 12.25. IR (KBr): $\nu(CO)$ 1942 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 334 cm^{-1}. ^{31}P NMR (32.44 MHz, CH_2Cl_2, −30 °C): δ 26.2 (d, $^2J_{PP}$ = 338 Hz, $P\frown O$), 15.1 (d, $^2J_{PP}$ = 338 Hz, $P\sim O$).

Carbonyl-*trans*-dichloro-*trans*-bis[(1,3-dioxoctane-2-ylmethyl)diphenylphosphine-*P;O′,P′*]ruthenium(II) (10b). **10b** was obtained as a yellow powder, mp 158–160 °C, in 66% yield. FD-MS: m/z 829 [M^+]. Anal. Calcd for $C_{39}H_{46}Cl_2O_5P_2Ru$: C, 56.52; H, 5.59; Cl, 8.55; Ru, 12.19. Found: C, 56.42; H, 5.67; Cl, 8.20; Ru, 11.70. IR (KBr): $\nu(CO)$ 1939 cm^{-1}. Far-IR (polyethylene): $\nu_{as}(RuCl_2)$ 335 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 24.4 (d, $^2J_{PP}$ = 335 Hz, $P\frown O$), 14.2 (d, $^2J_{PP}$ = 335 Hz, $P\sim O$).

Carbonylruthenium(II) Complexes *trans*-$Cl_2Ru(CO)(P\sim O)(P\frown O)$ (11b) and *cis,cis,trans*-$Cl_2Ru(CO)_2(P\sim O)_2$ (11e). Carbon monoxide was bubbled through a solution of 0.50 mmol of $Cl_2Ru(P\frown O)_2$ (**11a**) in dichloromethane (15 mL) at room temperature for 5 min, until the initial red solution had turned to orange. In contrast to the synthesis of **1b–10b**, with CO only *one* Ru-O bond in **11a** is cleaved to give $Cl_2Ru(CO)(P\sim O)(P\frown O)$ (**11b**). Dichloromethane was evaporated to low volume *in vacuo*. After *n*-hexane was added (10 mL) the orange precipitate was filtered off, washed with three portions (10 mL) of

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Table I. Coalescence Temperatures and Eyring Activation Parameters for Fluxional Processes in **1b–11b**, **1c–3c**

complex	T_c/K	$\Delta H^{\ddagger\,a}$/kJ mol^{-1}	$\Delta S^{\ddagger\,a}$/J mol^{-1} K^{-1}	$\Delta G_c^{\ddagger\,b}$/kJ mol^{-1}	$\Delta G^{\ddagger\,c}$/kJ mol^{-1}	ref
5b	247	24.4 ± 1.7	−80.6 ± 7.4	44.3 ± 2.5	48.4 ± 2.8	this work
2b	263	29.1 ± 2.0	−71.1 ± 8.2	47.8 ± 2.9	50.3 ± 3.1	13
3b	270	33.3 ± 1.4	−61.2 ± 5.3	49.8 ± 2.0	51.5 ± 2.1	13
4b	288	47.7 ± 3.4	−20.6 ± 12.7	53.6 ± 5.0	53.8 ± 5.1	12
10b	290	42.8 ± 3.6	−35.6 ± 12.8	53.1 ± 5.2	53.4 ± 5.2	this work
9b	303	51.9 ± 2.3	−14.3 ± 7.8	56.2 ± 3.3	56.1 ± 3.3	this work
8b	320	57.9 ± 3.7	−2.5 ± 12.2	58.7 ± 5.4	58.6 ± 5.2	this work
1b	328	59.5 ± 4.2	−2.7 ± 13.5	60.4 ± 6.1	60.3 ± 5.8	12
7b	349	68.8 ± 8.4	11.0 ± 26.4	65.0 ± 12.4	65.5 ± 11.5	this work
6b	355	68.9 ± 7.7^d	1.17 ± 23.2^d	68.5 ± 11.3^d	68.5 ± 10.3^d	12
11b^e	>373			69.2, 69.3^f		23
1c	348	70.0 ± 6.7	10.5 ± 19.6	66.4 ± 9.5	66.8 ± 8.9	13
2c	334	64.1 ± 4.0	−8.5 ± 12.3	66.9 ± 5.7	66.6 ± 5.4	13
3c^g	346			66.0^h		13

[a] Calculated at coalescence temperature (T_c) using a modified version of DNMR5,[21] and ACTPAR.[22] [b] Calculated at T_c using the required law of propagation of errors. [c] Calculated at 298 K using the required law of propagation of errors. [d] Due to overlapping signals of two diastereomers the calculation of correct values is prevented. [e] No data available because the complex decomposes at 373 K. [f] Calculated at 383 K (estimated T_c) using the approximate equation: $\Delta G^{\ddagger}{}_c = 19.14T_c(10.32 + \log T_c/k_c)$. [g] No data available because of the presence of four diastereomers. [h] Estimated from T_c using equation depicted in footnote *f*. Values of the other three diastereomers are 67.9, 68.4, and 68.8 kJ mol^{-1}.

Table II. Crystal Data for $RuCl_2(CO)(P\sim O)P\frown O)$ (**11b**)

formula	$C_{35}H_{42}Cl_4O_5P_2Ru$
fw	847.55
a, Å	11.974(2)
b, Å	10.877(2)
c, Å	29.567(6)
β, deg	96.34(3)
V, Å^3	3827.2(12)
cryst syst	monoclinic
space group	$P2_1/n$
Z	4
d_{calcd}, g/cm^3	1.471
μ(Mo Kα), mm^{-1}	0.803
λ, Å	0.710 73
temp, °C	−100
R^a	0.075
$R_w{}^b$	0.076

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

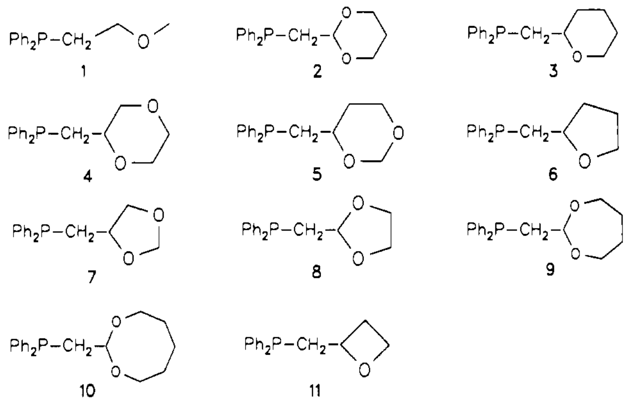

Figure 1. Schematic representation of the employed ether–phosphine ligands **1–11**.

n-hexane, and then dried in vacuo. Crystals of **11b** were obtained from a solution of chloroform/*n*-hexane which was allowed to stand under argon.

Only if the reaction is performed in an autoclave under CO pressure (60 bar, 80 °C, 2 h) the second Ru–O linkage splits to give ultimately the thermodynamically more stable *cis,cis,trans*-complex $Cl_2(CO)_2Ru(P\sim O)_2$ (**11e**). The working up has been performed as described above.

Carbonyl-*trans*-dichloro-*trans*-bis[(oxetane-2-ylmethyl)diphenylphosphine-*P*;*O′*,*P′*]ruthenium(II) (11b). **11b** was obtained as a yellow powder, mp 164–166 °C, in 73% yield. FD-MS: *m/z* 712 [M$^+$]. Anal. Calcd for $C_{33}H_{34}Cl_2O_3P_2Ru$: C, 55.68; H, 4.81; Cl, 9.96; Ru, 14.20. Found: C, 55.37; H, 4.76; Cl, 9.98; Ru, 13.78. IR (KBr): ν(CO) 1930 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 48.5, 46.9 (d, $^2J_{PP}$ = 346 Hz, $P\frown O$), 16.3, 17.8 (d, $^2J_{PP}$ = 346 Hz, $P\sim O$). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 22 °C): δ 204.73 (m, CO), 134.34–129.95 (m, C–Ph), 86.74 (s, CH, $P\frown O$), 79.41 (s, CH, $P\sim O$), 69.11 (s, OCH$_2$, $P\frown O$), 68.54 (s, OCH$_2$, $P\sim O$), 34.86 (m,[27] PCH$_2$, $P\frown O$), 31.59 (s, PCH$_2$CH*C*H$_2$, $P\frown O$), 28.42 (s, PCH$_2$CH*C*H$_2$, $P\sim O$), 27.75 (m,[27] PCH$_2$, $P\sim O$).

***cis*-Dicarbonyl-*cis*-dichloro-*trans*-bis[(oxetane-2-ylmethyl)diphenylphosphine-P]ruthenium(II) (11e).** **11e** was obtained as a colorless powder, mp 284–286 °C, in 58% yield. FD-MS: *m/z* 740 [M$^+$]. Anal. Calcd for $C_{34}H_{34}Cl_2O_4P_2Ru$: C, 55.19; H, 4.63; Cl, 9.58; Ru, 13.65. Found: C, 56.03; H, 4.30; Cl, 8.89; Ru, 14.58. IR (CH_2Cl_2): ν_{as}(CO) 1995, ν_s(CO) 2058 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30° C): δ 13.1 s, 13.5 s.

Carbonylruthenium(II) Complexes *cis*-$Cl_2Ru(CO)(P\sim O)(P\frown O)$ (1c–3c). The complexes $Cl_2Ru(CO)(P\sim O)(P\frown O)$ (**1b–3b**) (0.50 mmol) were dissolved in chloroform (25 mL) and the yellow solution refluxed (**1b**, 24 h; **2b**, 45 min; **3b**, 1 h). Dichloromethane was evaporated to low volume in vacuo. The yellow precipitate which formed immediately after addition of *n*-hexane was filtered off, washed with three portions (10 mL) of *n*-hexane, and dried in vacuo.

Carbonyl-*cis*-dichloro-*cis*-bis[(2-methoxyethyl)diphenylphosphine-*P*;*O′*,*P′*]ruthenium(II) (1c). **1c** was obtained as a yellow powder, mp 219 °C, in 86% yield. FD-MS: *m/z* 688 [M$^+$]. Anal. Calcd for $C_{31}H_{34}Cl_2O_3P_2Ru$: C, 54.08; H, 4.98; Cl, 10.30; Ru, 14.68. Found: C, 53.49; H, 4.86; Cl, 10.41; Ru, 14.62. IR (KBr): ν(CO) 1966 cm^{-1}. Far-IR (polyethylene): ν_{as}(RuCl$_2$) 308, ν_s(RuCl$_2$) 272 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 42.0 (d, $^2J_{PP}$ = 30 Hz, $P\frown O$), 41.0 (d, $^2J_{PP}$ = 30 Hz, $P\sim O$). ^{13}C NMR (100.61 MHz, $CDCl_3$, 22 °C): δ 196.26 (m, CO), 134.68–127.84 (m, C–Ph), 72.00 (s, CH$_2$O, $P\frown O$), 67.67 (s, CH$_2$O, $P\sim O$), 62.04 (s, OCH$_3$, $P\frown O$), 57.91 (s, OCH$_3$, $P\sim O$), 32.30 (m,[27] PCH$_2$, $P\frown O$), 29.88 (m,[27] PCH$_2$, $P\sim O$).

Carbonyl-*cis*-dichloro-*cis*-bis[(1,3-dioxane-2-ylmethyl)diphenylphosphine-*P*;*O′*,*P′*]ruthenium(II) (2c). **2c** was obtained as a yellow powder, mp 249 °C, in 79% yield. FD-MS: *m/z* 772 [M$^+$]. Anal. Calcd for $C_{35}H_{38}Cl_2O_5P_2Ru$: C, 54.41; H, 4.96; Cl, 9.18; Ru, 13.08. Found: C, 55.38; H, 5.04; Cl, 9.13; Ru, 12.39. IR (KBr): ν(CO) 1967 cm^{-1}. Far-IR (polyethylene): ν_{as}(RuCl$_2$) 308, ν_s(RuCl$_2$) 262 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 39.7 (d, $^2J_{PP}$ = 29 Hz, $P\frown O$), 32.8 (d, $^2J_{PP}$ = 29 Hz, $P\sim O$). ^{13}C NMR (100.61 MHz, $CDCl_3$, 22 °C): δ 196.21 (m, CO), 134.31–126.99 (m, C–Ph), 103.34 (s, CH, $P\frown O$), 99.07 (s, CH, $P\sim O$), 69.08 (s, RuOCH$_2$, $P\frown O$), 67.69 (s, OCH$_2$, $P\frown O$), 66.11 (s, OCH$_2$, $P\sim O$), 37.64 (m,[27] PCH$_2$, $P\frown O$), 34.81 (m,[27] PCH$_2$, $P\sim O$), 24.81 (s, OCH$_2$*C*H$_2$, $P\frown O$), 24.58 (s, OCH$_2$*C*H$_2$, $P\sim O$).

Carbonyl-*cis*-dichloro-*cis*-bis[diphenyl(tetrahydro-2H-pyran-2-ylmethyl)phosphine-*P*;*O′*,*P′*]ruthenium(II) (3c). **3c** was obtained as a yellow powder, mp 255 °C, in 85% yield. FD-MS: *m/z* 768 [M$^+$]. Anal. Calcd for $C_{37}H_{42}Cl_2O_3P_2Ru$: C, 57.82; H, 5.47; Cl, 9.23; Ru, 13.16. Found: C, 58.66; H, 6.24; Cl, 10.51; Ru, 12.87. IR (KBr): ν(CO) 1965 cm^{-1}. Far-IR (polyethylene): ν_{as}(RuCl$_2$) 304, ν_s(RuCl$_2$) 276 cm^{-1}. ^{31}P NMR (32.39 MHz, CH_2Cl_2, −30 °C): δ 44.0, 43.5, 43.4, 43.2 (d, $^2J_{PP}$ = 30, 31, 30, 29 Hz, $P\frown O$), 33.6, 40.2, 38.3, 38.9 (d, $^2J_{PP}$ = 30, 31, 30, 29 Hz, $P\sim O$). ^{13}C NMR (100.61 MHz, $CDCl_3$, 22 °C): δ 187.96 (m, CO), 135.55–126.96 (m, C–Ph), 78.35 (s, CH, $P\frown O$), 74.56 (s, CH, $P\sim O$), 71.75 (s, OCH$_2$, $P\frown O$), 67.44 (s, OCH$_2$, $P\sim O$), 41.15 (m,[27] PCH$_2$, $P\frown O$), 35.07 (m,[27] PCH$_2$, $P\sim O$), 33.03 (s, PCH$_2$CH*C*H$_2$), 25.34 [s, PCH$_2$CH(CH$_2$)$_2$*C*H$_2$], 23.31 (s, PCH$_2$CHCH$_2$*C*H$_2$).

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\mathrm{pm}^2 \times 10^{-1}$)

atom	x	y	z	U_{eq}[a]
Ru(1)	440(1)	1654(1)	1213(1)	20(1)
C(1)	29(8)	3092(10)	1442(3)	23(2)
O(1)	−208(6)	4034(7)	1592(2)	37(2)
Cl(1)	1287(2)	907(2)	1930(1)	29(1)
Cl(2)	−303(2)	2037(3)	443(1)	33(1)
P(1)	2190(2)	2425(2)	1062(1)	23(1)
P(2)	−1295(2)	684(2)	1320(1)	23(1)
O(2)	1159(6)	−25(7)	971(2)	29(2)
O(3)	−3726(7)	3122(8)	767(3)	46(2)
C(2)	2788(9)	1120(10)	777(4)	31(3)
C(3)	2385(10)	−99(11)	944(4)	37(3)
C(4)	2184(10)	−1106(11)	587(4)	36(3)
C(5)	945(10)	−813(12)	567(4)	46(3)
C(6)	−2544(9)	1275(10)	976(4)	31(3)
C(7)	−2674(10)	2664(11)	1035(4)	39(3)
C(8)	−3055(12)	3209(14)	1456(5)	59(4)
C(9)	−3919(12)	3889(14)	1132(4)	56(4)
C(10)	3913(6)	2017(4)	1773(2)	35(3)
C(11)	4707	2396	2127	45(3)
C(12)	4805	3639	2241	42(3)
C(13)	4109	4503	2002	40(3)
C(14)	3316	4124	1649	31(3)
C(15)	3217	2881	1534	26(3)
C(16)	3238(5)	3891(6)	462(2)	32(3)
C(17)	3310	4890	171	38(3)
C(18)	2405	5696	87	41(3)
C(19)	1427	5503	293	35(3)
C(20)	1355	4503	584	30(3)
C(21)	2260	3697	669	26(2)
C(22)	−1863(6)	−1355(6)	753(2)	38(3)
C(23)	−1796	−2593	636	49(3)
C(24)	−1164	−3405	926	45(3)
C(25)	−599	−2978	1334	45(3)
C(26)	−666	−1740	1451	32(3)
C(27)	−1297	−928	1161	21(2)
C(28)	−1273(5)	1499(6)	2223(2)	29(3)
C(29)	−1670	1549	2649	31(3)
C(30)	−2535	768	2747	37(3)
C(31)	−3003	−63	2420	41(3)
C(32)	−2605	−113	1995	31(3)
C(33)	−1741	668	1896	22(2)
C(50)	2763(11)	−1838(12)	2253(4)	50(3)
Cl(3)	2319(4)	−2728(4)	1780(2)	97(2)
Cl(4)	4106(3)	−1235(4)	2212(2)	90(2)
O(5)	5086(9)	8303(10)	1130(4)	74(3)
C(60)	4976(8)	7830(9)	246(3)	21(2)
O(60)	5173(9)	9046(10)	194(4)	80(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Data Collection, Structure Solution, and Refinement. A suitable crystal with approximate dimensions 0.2 × 0.25 × 0.5 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer with low-temperature equipment. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters are summarized in Table II. Intensities were collected with graphite-monochromatized Mo Kα radiation using the ω-scan technique with scan speeds varying from 10 to 30°/min in ω. Two check reflections were monitored after every 58 intensity measurements. The usual corrections for Lorentz and polarization effects were applied to intensity data. An absorption correction was applied (Ψ-scan, maximum and minimum transmission, 0.657 and 0.558, respectively). The structure was solved by direct methods[29] and refined by the full-matrix least-squares method. The ruthenium, phosphorus, and chlorine atoms were refined anisotropically. Hydrogen atoms were in calculated positions (riding model, hydrogen atoms of O(5) and O(60) not included) and the phenyl substituents were treated as rigid groups. The crystal contains one solvent molecule of CH_2Cl_2, CH_3OH, and OH_2, respectively. Maximum and minimum peaks in the final difference synthesis (located arround O(5)) were 4.16 and −0.67 e Å^{-3}, respectively. Final atomic coordinates are given in Table III.

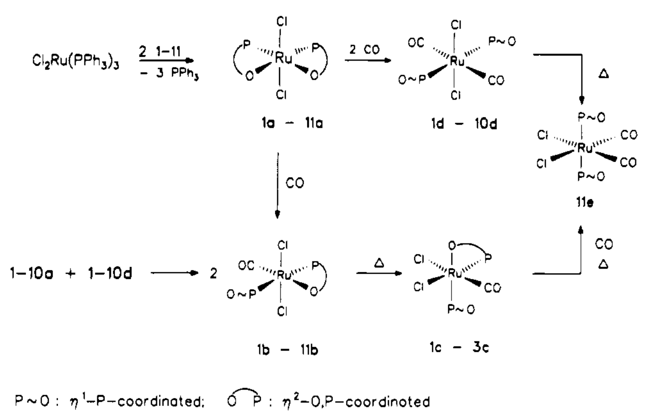

Figure 2. Schematic representation of the synthesis of the various types of (ether–phosphine)ruthenium(II) complexes.

Results and Discussion

Synthesis. Reaction of the ether-phosphines **1**-**11** (Figure 1) with $Cl_2Ru(PPh_3)_3$ results in the formation of the bis(chelate) complexes *trans*-$Cl_2Ru(\mathrm{P}\frown\mathrm{O})_2$ (**1a**-**11a**) ($\mathrm{P}\sim\mathrm{O} = \eta^1$-P-coordinated; $\mathrm{P}\frown\mathrm{O} = \eta^2$-O,P-coordinated). With CO both Ru–O bonds are cleaved to give *all-trans*-$Cl_2(OC)_2Ru(\mathrm{P}\sim\mathrm{O})_2$ (**1d**–**4d**;[13,24] **6d**;[25] **8d**; **5**, **7**, **9**, **10d** only in solution) (Figure 2). The complexes **1b**–**10b** which show fluxional behavior are obtained from stoichiometric amounts of the bis(chelate) complexes **1a**–**10a** and the dicarbonyl species **1d**–**10d** (Figure 2). In contrast to these results, with CO only one Ru–O bond in **11a** is ruptured to form $Cl_2Ru(CO)(\mathrm{P}\frown\mathrm{O})(\mathrm{P}\sim\mathrm{O})$ (**11b**) (Figure 2). Only if the reaction is performed in an autoclave under CO pressure (60 bar, 80 °C, 2 h) the second Ru–O linkage splits to give ultimately the thermodynamically more stable *cis,cis,trans*-complex $Cl_2(OC)_2Ru(\mathrm{P}\sim\mathrm{O})_2$ (**11e**) (Figure 2). Upon heating the kinetically controlled products **1b**–**3b** are transformed into the thermodynamically stable isomers *cis*-$Cl_2Ru(CO)(\mathrm{P}\sim\mathrm{O})(\mathrm{P}\frown\mathrm{O})$ (**1c**–**3c**) (Figure 2).

Spectroscopic Data. The IR, far-IR, and ^{31}P NMR spectra of the synthesized complexes **5a**,**b**, **7a**,**b**–**10a**,**b**, **8d**, and **11e** are comparable to well-known (ether–phosphine)ruthenium(II) complexes.[13,23-26] Although in contrast to **3**–**7** and **11**, the ether-phosphines **8** and **9** do not have a chiral C atom, the bis(chelate) complexes **8a** and **9a** show two singlets in the ^{31}P NMR spectra at −30 °C due to two diastereomers which are caused by C chirality, resulting from η^2-complexation of the O,P ligand.

Dynamic Behavior and Variable-Temperature ^{31}P NMR Studies of 1b–11b and 1c–3c. The temperature-dependent ^{31}P NMR spectra of **1c**–**3c** and **1b**–**11b** indicate that the compounds are fluxional in solution. Whereas at higher temperatures one signal is always observed, at low temperatures the spectra display typical AB patterns (Figure 3). The large coupling constants of $^2J(PP) \approx 340$ Hz are consistent with two trans-phosphorus atoms in **1b**–**11b**. In contrast the small coupling constants of $^2J(PP) \approx 30$ Hz in **1c**–**3c** demonstrate the cis-position of the P atoms. As the temperature is raised, the two doublets first broaden, then coalesce (Table I), and finally become a sharp singlet. This averaging of magnetic environments on the NMR time scale at higher temperatures indicates that the two O,P ligands undergo mutual exchange. The two exchange mechanisms shown in Figure 4 involve primarily cleavage of one Ru-O bond (**b**, **c**), followed by rearrangement of the resulting five-coordinate ruthenium unit (only in the case of **c**), and finally recombination of the Ru–O bond (**b**, **c**). All phenomena are reversible. No discernible trans-cis isomerization $\mathbf{b} \Rightarrow \mathbf{c}$ is observed while the spectra were recorded. Because strongly coordinating solvents like tetrahydrofuran or dioxane could influence the exchange, chloroform or 1,1′,2,2′-tetrachloroethane were employed. The coalescence temperatures were not affected by using these two solvents.

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(29) SHELXTL-PC version 4.2. Sheldrick, G. M. University of Göttingen.

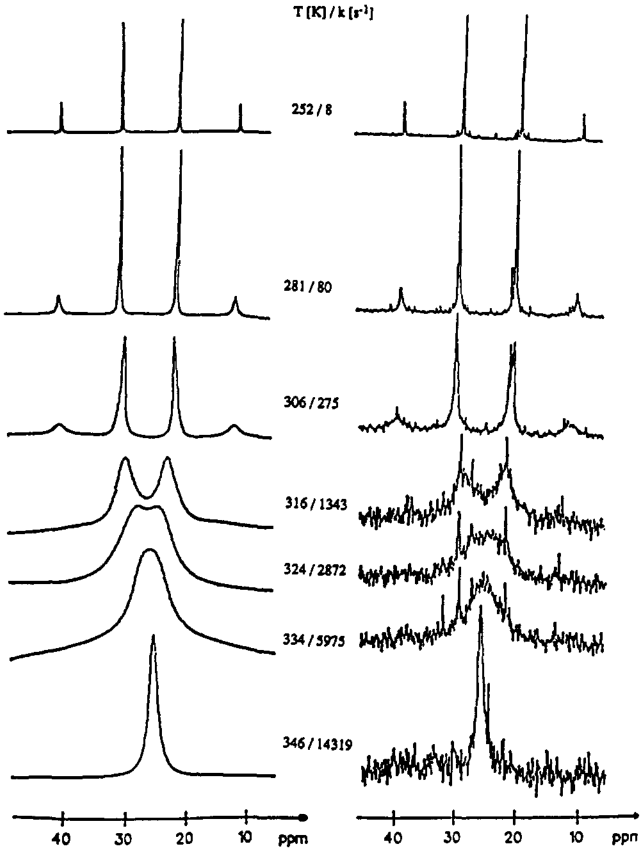

Figure 3. Experimental and computer-simulated variable-temperature ^{31}P NMR spectra and rate constants, *k*, for O,P exchange in $Cl_2Ru(CO)(P\sim O)(P\frown O)$ (**8b**).

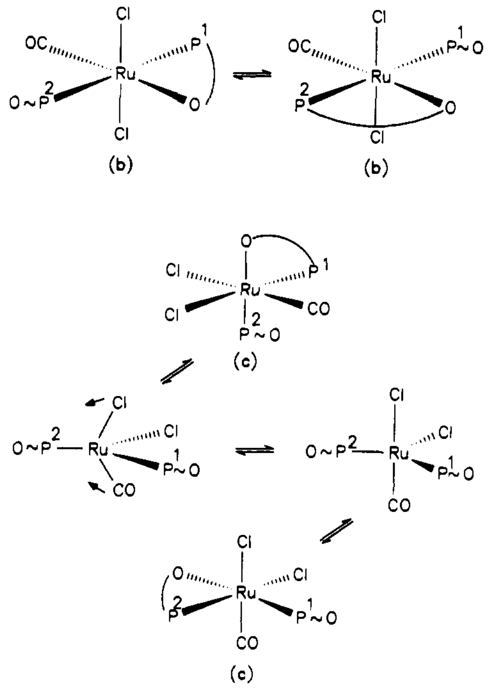

Figure 4. Schematic representation of the two mechanisms of fluxionality for the isomeric structures of the complexes $Cl_2Ru(CO)(P\sim O)(P\frown O)$ (**1b–11b**, **1c–3c**).

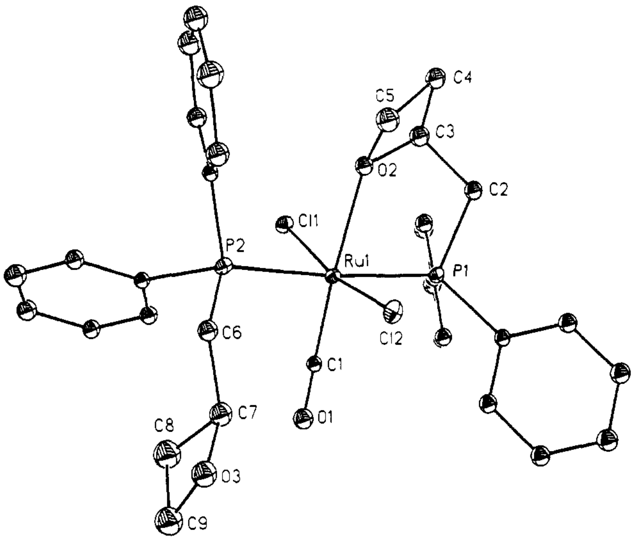

Figure 5. ORTEP plot of **11b**.

Table IV. Selected Bond Distances (pm) and Angles (deg) for **11b**

	Distances		
Ru(1)–Cl(2)	239.0(3)	Ru(1)–Cl(1)	238.7(3)
Ru(1)–P(2)	238.2(3)	Ru(1)–P(1)	234.6(3)
Ru(1)–C(1)	179.3(10)	Ru(1)–O(2)	217.4(7)
O(2)–C(3)	148.1(14)	O(2)–C(5)	147.0(14)
O(3)–C(7)	149.9(14)	O(3)–C(9)	140.2(16)
	Angles		
P(1)–Ru(1)–P(2)	173.8(1)	Cl(1)–Ru(1)–Cl(2)	169.2(1)
C(1)–Ru(1)–O(2)	172.6(4)	P(1)–Ru(1)–O(2)	80.9(2)
C(3)–O(2)–C(5)	90.5(8)	C(7)–O(3)–C(9)	89.5(8)

Using a modified version of DNMR5,[21] 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. Graphic application of the Eyring equation to the kinetic data involving a nonlinear least-squares program (ACTPAR[22]) afforded the thermodynamic parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G_c^{\ddagger}$, and $\Delta G_{298}^{\ddagger}$. In most cases the entropies show small positive or negative values, thus indicating an intramolecular exchange.[30,31] $\Delta G^{\ddagger}$ is regarded as the difference between the ground-state and transition-state energies, while $\Delta H^{\ddagger}$ is an indication of the Ru–O bond strength. The calculated values of $\Delta H^{\ddagger}$ in **1b–11b** correlate with the ability of O atoms in noncoordinated cyclic ethers to act as donors. These values increase with decreasing ring size of the ethers ($4 > 5 > 7 \approx 8 > 6$).[32–34] The complexes **2b–5b**, **9b**, and **10b** provided with larger O,P ligands exhibit lower barriers than the other complexes **1b**, **6b–8b**, and **11b** with smaller ether-phosphines. This can be rationalized by proposing that the steric demand of the ligands in the transition state is less significant than that in the ground state. In that case the bulky O,P ligands would sterically destabilize the ground state relative to the transition state, hence reducing the barriers of fluxionality.[35] The higher barriers for the exchange in **1c–3c** compared to **1b–3b** are not surprising in view of the rearrangement of the ligands, which requires additional energy. The differences of $\Delta H^{\ddagger}$ between the two isomers **b**,**c** increase with increasing mass of the ligand ($\Delta H^{\ddagger}$: **1c–1b** > **2c–2b** > **3c-3b**). Complex **11b** with the strong basic ether–phosphine ligand **11** is subject to decomposition before achieving coalescence, hence dynamic behavior could not be investigated.

Molecular Structure of 11b. An X-ray crystallographic study of **11b** has been carried out. Crystal structure parameters are given in Table II; atomic positions and selected bond lengths and angles are listed in Tables III and IV. Perspective view of the

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molecule is depicted in Figure 5. The angles P(1)–Ru(1)–O(2) and C(1)–Ru(1)–Cl(2) differ widely from 90°. The Ru(1)–O(2) bond length (217.2 pm) is significantly shorter (10 pm) compared to those for other (ether–phosphine)ruthenium(II) complexes[13,25,26] and clearly illustrates the strong basic properties of the four-membered cyclic ether. Both rings (P∼O, P⌒O) are nearly planar.

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Supplementary Material Available: A figure showing the molecular structure of **11b** with the complete labeling scheme and tables giving the structure determination summary, anisotropic temperature factors, and hydrogen atom parameters (6 pages). Ordering information is given on any current masthead page.