

Synthesis, Reactivity, and Structural Characterization of Octahedral Ruthenium(II) Complexes with Small Molecules Containing Hemilabile Ether–Phosphine Ligands[†]

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Received April 26, 1995[§]

The octahedrally coordinated bis(ether–phosphine)ruthenium(II) complexes $\text{Cl}_2\text{Ru}(\text{P}^{\sim}\text{O})_2$ (**1a–c**) (P^{\sim}O , $\eta^2(\text{O,P})$ -chelated ether–phosphine; **a**, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$; **b**, $\text{Ph}_2\text{PCH}_2\text{C}_4\text{H}_7\text{O}_2$; **c**, $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$) represent potentially unsaturated 14-electron metal species which are weakly protected by intramolecular chelation of the ether moiety. The ease of Ru–O bond cleavage is shown by the reaction with a variety of small molecules. Sulfur dioxide, acetonitrile, and *tert*-butyl isocyanide are readily added to **1a–c** to generate the corresponding complexes $\text{Cl}_2\text{Ru}(\text{P}^{\sim}\text{O})(\text{P}^{\sim}\text{O})(\eta^1\text{-SO}_2)$ (**2a–c**) (P^{\sim}O , $\eta^1(\text{P})$ -coordinated ether–phosphine), $\text{Cl}_2\text{Ru}(\text{CH}_3\text{CN})(\text{P}^{\sim}\text{O})(\text{P}^{\sim}\text{O})$ (**4a–c**), and $\text{Cl}_2\text{Ru}(\text{CNCMe}_3)_2(\text{P}^{\sim}\text{O})_2$ (**8a–c**), respectively. The action of carbon disulfide on **1c** affords an insertion into the Ru–P bond to give the phosphoniodithiocarboxylato complex $\text{Cl}_2\text{Ru}(\text{S}_2\text{CP}^{\sim}\text{O})(\text{P}^{\sim}\text{O})$ (**5c**). Phenylacetylene is activated by the starting complexes **1a–c** to yield the vinylidene compounds $\text{Cl}_2\text{Ru}(\text{C}=\text{CHPh})(\text{P}^{\sim}\text{O})(\text{P}^{\sim}\text{O})$ (**3a–c**). All complexes are accessible under moderate reaction conditions in almost quantitative yields. The fluxional behavior of a variety of substrate complexes in solution was investigated by temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Remarkably, the vinylidene complexes **3a,b** show complex exchange phenomena which account for two dynamic processes. The structures of **2a**, **3a**, **3c**, *trans*- $\text{Cl}_2\text{Ru}(\text{CNCMe}_3)(\text{P}^{\sim}\text{O})(\text{P}^{\sim}\text{O})$ (**9a**), and *cis*- $\text{Cl}_2\text{Ru}(\text{CNCMe}_3)(\text{P}^{\sim}\text{O})(\text{P}^{\sim}\text{O})$ (**10b**) were determined by single-crystal X-ray diffraction. Aside from the coordinated small molecules, the structures of **3c** and **9a** are similar with *trans*-arranged phosphines, whereas **2a**, **3a**, and **10b** are set up with *cis*-positioned phosphines. **2a** and **10b** crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$, and **3a**, **3c**, and **9a** have the triclinic space group $P\bar{1}$ with $Z = 2$. The cell dimensions are as follows: for **2a**, $a = 18.991(7)$ Å, $b = 9.717(3)$ Å, $c = 19.930(6)$ Å, $\beta = 110.94(3)^\circ$; for **3a**, $a = 9.687(1)$ Å, $b = 11.768(2)$ Å, $c = 16.386(2)$ Å, $\alpha = 103.08(1)^\circ$, $\beta = 103.84(1)^\circ$, $\gamma = 91.37(1)^\circ$; for **3c**, $a = 12.420(2)$ Å, $b = 12.621(2)$ Å, $c = 13.556(2)$ Å, $\alpha = 91.66(3)^\circ$, $\beta = 101.34(3)^\circ$, $\gamma = 110.11(3)^\circ$; for **9a**, $a = 9.416(2)$ Å, $b = 12.791(2)$ Å, $c = 15.665(4)$ Å, $\alpha = 79.39(2)^\circ$, $\beta = 76.59(2)^\circ$, $\gamma = 78.43(1)^\circ$; for **10b**, $a = 9.870(3)$ Å, $b = 11.171(4)$ Å, $c = 34.778(14)$ Å, $\beta = 93.27(4)^\circ$.

Introduction

Coordinationally unsaturated transition metal complexes are of continual growing interest during the last few years.¹ The deficiency of ligands makes them available as valuable precursors in catalytically operating processes.² In particular, with the elements ruthenium and osmium, there are well-known 16-electron complexes with sterically encumbered phosphine ligands.^{1a–d}

For further stabilization we recently introduced bifunctional ether–phosphines (O,P) acting as monodentate (P^{\sim}O) or bidentate (P^{\sim}O) ligands, respectively. These ligands are set up with oxygen donors incorporated in cyclic or linear ether moieties providing a weak metal–oxygen bond and a phosphorus atom closely coordinated to the central atom. Due to

the hemilabile character, the ether oxygen donor may be regarded as an intramolecular solvent molecule, both avoiding decomposition and preserving increased reactivity of organometallic species, rather than simple solvent adducts.³

Recently we have reported about the fluxional behavior of octahedral ruthenium(II) complexes containing both monodentate (P^{\sim}O) and bidentate (P^{\sim}O) ether–phosphines ($\text{P}^{\sim}\text{O} = \eta^1(\text{P})$ -coordinated ligand; $\text{P}^{\sim}\text{O} = \eta^2(\text{O,P})$ -chelated ligand), and we were able to present thermodynamic parameters for the ruthenium–oxygen contact.⁴ The strength of the metal–oxygen bond depends on the O nucleophilicity, the ring size of the cyclic ether, the number and position of the oxygen atoms in the ring, and the basicity at the ruthenium center controlled by the donor ability of the phosphines.^{4,5} To sum up these examinations it can be said that six-membered ether moieties containing two oxygen atoms are of least donor strength, whereas the open-chain methoxyethyl ether shows an average basicity. On the basis of these experimental results, we draw our attention to the investigation of the chemical reactivity of octahedral bis-(η^2 -ether–phosphine)ruthenium(II) complexes toward small molecules. These complexes behave as 14e-ruthenium(II) fragments weakly protected by intramolecular coordination of the ether moiety.

[†] Dedicated to Professor William C. Kaska on the occasion of his 60th birthday.

[§] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

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This article reports about reactive bis(chelate)ruthenium(II) complexes $[\text{RuCl}_2(\text{P}^{\sim}\text{O})_2]$ (**1a–c**) having two pseudovacant coordination sites at the ruthenium center, due to two weak Ru–O interactions. A facile cleavage of one or both ruthenium–oxygen bonds is achieved by reaction with small molecules such as sulfur dioxide, carbon disulfide, acetonitrile, phenylacetylene, and isocyanide. Moreover we employed three different ether–phosphines in order to investigate the dependence of the reactivity of the complexes **1a–c** on the strength of the ruthenium–oxygen bond.

Experimental Section

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. The photochemical reaction was carried out with a water-cooled reactor containing an Original Hanau TQ 150 Hg lamp. 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 (35 °C), modified by AMD; FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (NBA matrix, 50 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; Cl and S analyses were carried out according to Schöniger,⁶ Cl was analyzed as described by Dirscherl and Erne,⁷ and S was analyzed as described by Wagner.⁸ Ru was determined according to the literature.⁹ $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on Bruker WP 80, Bruker AC 80, and Bruker AMX 400 instruments operating at 32.39, 32.44, and 161.98 MHz, respectively, with external standard at low temperatures (0 to –80 °C) 1% H_3PO_4 in acetone- d_6 and above 0 °C 1% H_3PO_4 in D_2O . ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR used Bruker AC 80, Bruker AC 250, and Bruker AMX 400 instruments at 80.13 and 20.15, 250.13 and 62.90, and 400.13 and 100.62 MHz, respectively. The temperatures of the variable-temperature ^{31}P NMR spectra were calibrated using the method of van Geet¹⁰ and are considered accurate to ± 1 K. ^1H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to Me_4Si . The starting complexes **1a**, **b**¹¹ and the ether–phosphine $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ ¹² were synthesized according to the literature.

trans-Dichloro-cis-bis[dicyclohexyl(methoxyethyl)phosphine-O,P]-ruthenium(II) (1c). A 2.00 mmol sample (512.7 mg) of $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ was dissolved in dichloromethane (10 mL) and added with stirring to a solution of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ (959.0 mg, 1.00 mmol) in dichloromethane (20 mL). After the mixture was refluxed for 15 min, the solvent was removed under reduced pressure and the oily residue was purified by chromatography on activated silica gel (length of column 20 cm). PPh_3 was eluted with diethyl ether as eluent. The purple fraction which contained **1c** was eluted with 1/5 CH_2Cl_2 /diethyl ether and evaporated to dryness. The remaining solid **1c** was obtained as a bright purple powder: yield 75%; mp 155 °C dec. FD-MS: m/z 684 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{30}\text{H}_{58}\text{Cl}_2\text{O}_2\text{P}_2\text{Ru}$: C, 52.62; H, 8.54; Cl, 10.36; Ru, 14.76. Found: C, 52.57; H, 8.53; Cl, 10.40; Ru, 15.20. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{C}_2\text{O})$ 1075 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30 °C): δ 61.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, C_6D_6 , 22 °C): δ 72.3 (s, OCH_3), 62.0 (s, OCH_3), 37.8 (m, ^{13}C J = 10.2 Hz, PCH), 30.3–26.9 (m, CH_2 of C_6H_{11}), 25.3 (m, ^{13}C J = 10.5 Hz, PCH_2).

cis-Dichloro-cis-bis[(methoxyethyl)diphenylphosphine-P;O',P']-(η^1 -sulfur dioxide-S)ruthenium(II) (2a). Sulfur dioxide was bubbled into a solution of **1a** (500 mg, 0.76 mmol) dissolved in 20 mL of dichloromethane at ambient temperature. An immediate color change

from red to orange occurred. After 15 min of stirring under an SO_2 atmosphere, the solvent was removed under vacuum. The residue was washed with 10 mL of *n*-hexane to give a yellow precipitate. Crystallization of the crude product from CH_2Cl_2 /diethyl ether both saturated with sulfur dioxide resulted in precipitation of orange crystals of **2a**·0.25 CH_2Cl_2 : yield 80%; mp 168 °C dec. FD-MS: m/z 689 $[\text{M}^+ - \text{Cl}]$. Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{O}_4\text{P}_2\text{RuS}$ ·0.25 CH_2Cl_2 : C, 48.71; H, 4.66; Cl, 11.88; S, 4.30; Ru, 13.55. Found: C, 48.85; H, 4.79; Cl, 11.95; S, 4.74; Ru, 13.82. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{SO}_2)$ 1289 (s), $\nu_{\text{s}}(\text{SO}_2)$ 1123 (vs). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30 °C): δ 35.1 (d, $^2J_{\text{PP}}$ = 27 Hz, P^{\sim}O), 29.2 (d, $^2J_{\text{PP}}$ = 27 Hz, P^{\sim}O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl_3 , –30 °C): δ 135.5–127.4 (m, C–Ph), 71.5 (s, OCH_2CH_2 , P^{\sim}O), 67.5 (s, OCH_2CH_2 , P^{\sim}O), 61.2 (s, OCH_3 , P^{\sim}O), 58.2 (s, OCH_3 , P^{\sim}O), 31.2 (m, PCH_2 , P^{\sim}O), 29.5 (m, PCH_2 , P^{\sim}O).

cis-Dichloro-cis-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P;O',P']-(η^1 -sulfur dioxide-S)ruthenium(II) (2b). Sulfur dioxide was bubbled into a solution of **1b** (450 mg, 0.60 mmol) dissolved in 25 mL of THF. The SO_2 stream was maintained, and the mixture was refluxed for 1 h. During that time a color change from red to orange occurred. Yellow crystals were precipitated while the solution was cooled to ambient temperature. The crystals were separated and dried in vacuo. Crystallization from CH_2Cl_2 /diethyl ether yields 83% of **2b**·0.5 CH_2Cl_2 , mp 214 °C dec. FAB-MS: m/z 773 $[\text{M}^+ - \text{Cl}]$. Anal. Calcd for $\text{C}_{34}\text{H}_{38}\text{Cl}_2\text{O}_6\text{P}_2\text{RuS}$ ·0.5 CH_2Cl_2 : C, 48.69; H, 4.62; Cl, 12.50; S, 3.77; Ru, 11.87. Found: C, 48.97; H, 4.79; Cl, 12.17; S, 3.40; Ru, 12.25. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{SO}_2)$ 1297 (s), $\nu_{\text{s}}(\text{SO}_2)$ 1125 (vs). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30 °C): δ 39.0 (d, $^2J_{\text{PP}}$ = 28 Hz, P^{\sim}O), 30.4 (d, $^2J_{\text{PP}}$ = 28 Hz, P^{\sim}O). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.90 MHz, CDCl_3 , 22 °C): δ 134.8–127.9 (m, C–Ph), 103.9 (s, CH_2CH , P^{\sim}O), 99.8 (s, CH_2CH , P^{\sim}O), 68.0 (m, OCH_2CH_2 , P^{\sim}O), 66.9 (m, OCH_2CH_2 , P^{\sim}O), 36.2 (m, PCH_2 , P^{\sim}O), 35.7 (m, PCH_2 , P^{\sim}O), 25.9 (s, OCH_2CH_2 , P^{\sim}O), 25.6 (s, OCH_2CH_2 , P^{\sim}O).

trans-Dichloro-trans-bis[dicyclohexyl(methoxyethyl)phosphine-P;O',P']-(η^1 -sulfur dioxide-S)ruthenium(II) (2c). A suspension of **1c** (450 mg, 0.66 mmol) in liquid sulfur dioxide (10 mL) was stirred at –15 °C. After 15 min a color change from dark purple to red occurred. Excess sulfur dioxide was removed by increasing the temperature up to –5 °C. The residue was washed with two portions of *n*-pentane at –5 °C to give an orange powder, which was collected by filtration (G 3) and dried in an argon stream: yield 90% of **2c**; mp 192 °C dec. FD-MS: m/z 751 $[\text{M}^+]$. Anal. Calcd for $\text{C}_{30}\text{H}_{58}\text{Cl}_2\text{O}_4\text{P}_2\text{RuS}$: C, 48.12; H, 7.81; Cl, 9.47; S, 4.28; Ru, 13.50. Found: C, 47.88; H, 7.66; Cl, 9.64; S, 4.80; Ru, 13.05. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{SO}_2)$ 1286 (s), $\nu_{\text{s}}(\text{SO}_2)$ 1120 (vs). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, acetone, –30 °C): δ 50.5 (d, $^2J_{\text{PP}}$ = 288 Hz, P^{\sim}O), 29.2 (d, $^2J_{\text{PP}}$ = 288 Hz, P^{\sim}O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl_3 , –30 °C): δ 67.7 (s, OCH_2CH_2 , P^{\sim}O), 65.3 (s, OCH_2CH_2 , P^{\sim}O), 58.0 (s, OCH_3 , P^{\sim}O), 56.5 (s, OCH_3 , P^{\sim}O), 34.6 (m, PCH , P^{\sim}O), 33.4 (m, PCH , P^{\sim}O), 28.9–24.4 (m, CH_2 of C_6H_{11}), 18.9 (m, PCH_2 , P^{\sim}O), 17.9 (m, PCH_2 , P^{\sim}O).

(Benzylidenecarbene)-cis-dichloro-cis-bis[(methoxyethyl)diphenylphosphine-P;O',P']ruthenium(II) (3a). Phenylacetylene (153 mg, 1.50 mmol) was added to a solution of **1a** (620 mg, 0.94 mmol) in 25 mL of dichloromethane. After the mixture was refluxed for 30 min, the red-brown solution was evaporated to dryness. The residue was washed three times with diethyl ether (each 10 mL) to give an orange-brown precipitate, which was collected by filtration (G 3), and dried in vacuo. Crystals from **3a** were obtained from CH_2Cl_2 /diethyl ether by slow diffusion: yield 95%; mp 151 °C. FAB-MS: m/z 727 $[\text{M}^+ - \text{Cl}]$. Anal. Calcd for $\text{C}_{38}\text{H}_{40}\text{Cl}_2\text{O}_2\text{P}_2\text{Ru}$: C, 59.85; H, 5.29; Cl, 9.30; Ru, 13.25. Found: C, 60.28; H, 5.22; Cl, 9.83; Ru, 13.15. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{C})$ 1592 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2 , –19 °C): isomer I, δ 36.4, 36.1 (each d, AB system, $^2J_{\text{PP}}$ = 32.6 Hz); isomer II, δ 44.2 (d, $^2J_{\text{PP}}$ = 24.4 Hz, P^{\sim}O), 28.9 (d, $^2J_{\text{PP}}$ = 24.4 Hz, P^{\sim}O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl_3 , –30 °C): δ 356.7 (m, ^{13}C J = 17.7 Hz, $\text{Ru}=\text{C}$), 135.4–125.1 (m, C–Ph), 111.9 (s, $=\text{CHPh}$), 77.0 (s, OCH_2CH_2 , P^{\sim}O), 75.4 (s, OCH_2CH_2 , P^{\sim}O), 62.4 (s, OCH_3 , P^{\sim}O), 57.9 (s, OCH_3 , P^{\sim}O), 30.7 (m, PCH_2 , P^{\sim}O), 30.0 (m, PCH_2 , P^{\sim}O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CD_2Cl_2 , 30 °C): δ 356.0 (m, ^{13}C J = 18.2 Hz, $\text{Ru}=\text{C}$), 135.5–125.6 (m, C–Ph), 112.9 (s, $=\text{CHPh}$), 70.1 (m, OCH_2CH_2), 59.7 (m, OCH_3), 28.7 (m, PCH_2). ^1H NMR (400.13 MHz, CD_2Cl_2 , –19 °C): δ 7.88–6.60 (m, C_6H_5); isomer I, δ 5.32 (m, ^{13}C J

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(13) A part of an AXX' spectrum, $J = |^1J_{\text{PC}} + ^3J_{\text{PC}}|$.

(14) A part of an AXY' spectrum, $J = |^2J_{\text{PC}} + ^2J_{\text{PC}}|$.

1.0 Hz, =CHPh); isomer II, δ 5.19 (m, $^{15}J = 3.3$ Hz, =CHPh); δ 3.82 (m, CH₂OCH₃); 3.41–2.91 (m, OCH₃); 2.61–2.18 (m, PCH₂).

(Benzylidenecarbene)-cis-dichloro-cis-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P;O',P']ruthenium(II) (3b). A suspension of **1b** (550 mg, 0.74 mmol) and 20 mL of toluene was treated with phenylacetylene (153 mg, 1.5 mmol). The mixture was refluxed for 1 h; during that time the solid stuff dissolved, and the color changed from red to orange-brown. The solution was cooled to room temperature and evaporated to dryness. The brown residue was stirred with diethyl ether (2 \times 15 mL) to yield an orange-brown precipitate, which was crystallized from CH₂Cl₂/diethyl ether by slow diffusion. The red crystals were collected and dried in vacuo: yield 68% of **3b**; mp 172 °C dec. FAB-MS: m/z 811 [M⁺ – Cl]. Anal. Calcd for C₄₂H₄₄Cl₂O₄P₂Ru: C, 59.58; H, 5.24; Cl, 8.37; Ru, 11.94. Found: C, 59.59; H, 5.56; Cl, 7.90; Ru, 11.60. IR (KBr, cm⁻¹): ν (C=C) 1593 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH₂Cl₂, –30 °C): isomer I, δ 29.8, 28.6 (each d, AB system, $^2J_{\text{PP}} = 24$ Hz); isomer II, δ 39.2 (d, $^2J_{\text{PP}} = 32$ Hz, P[–]O), 21.2 (d, $^2J_{\text{PP}} = 32$ Hz, P[–]O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl₃, –30 °C): δ 354.0 (m, $^{14}J = 17.0$ Hz, Ru=C), 134.8–125.2 (m, C–Ph), 111.8 (s, =CHPh), 103.3 (s, CH₂CH, P[–]O), 99.4 (s, CH₂CH, P[–]O), 70.3 (m, OCH₂CH₂, P[–]O), 66.5 (m, OCH₂CH₂, P[–]O), 37.9 (m, PCH₂, P[–]O), 34.0 (m, PCH₂, P[–]O), 24.9 (s, OCH₂CH₂, P[–]O), 22.3 (s, OCH₂CH₂, P[–]O). ^1H NMR (80.13 MHz, CDCl₃, –30 °C): δ 7.86–6.61 (m, 25 H, C₆H₅), 5.42 (m, 1 H, =CHPh), 5.27 (m, 1 H, CH₂CH, P[–]O), 4.35 (m, 1 H, CH₂CH, P[–]O), 4.00–0.77 (m, 16 H, alkanes).

(Benzylidenecarbene)-trans-dichloro-trans-bis[dicyclohexyl(methoxyethyl)phosphine-P;O',P']ruthenium(II) (3c). **Method a.** A solution of **1c** (310 mg, 0.45 mmol) in 10 mL of toluene was treated with phenylacetylene (92 mg, 0.90 mmol), and heated under reflux for 2 h. After cooling to room temperature, the solution was concentrated to 1 mL under reduced pressure, and then chromatographed on activated silica gel (column length 25 cm). A yellow-orange fraction was eluted with 4/1 *n*-hexane/acetone and evaporated to dryness. The orange residue was washed with *n*-pentane (10 mL) and collected by filtration (G 3) to yield 55% of an orange powder of **3c**, mp 152 °C dec. FD-MS: $m/z = 786$ [M⁺].

Method b. **1c** (500 mg, 0.73 mmol) and phenylacetylene (150 mg, 1.47 mmol) were dissolved in 15 mL of toluene and irradiated at ambient temperature with a 150-W Hg lamp. The red solution was concentrated to 1 mL under reduced pressure and purified as mentioned above to give an orange powder of **3c**: yield 90%; mp 153 °C. FD-MS: m/z 786 [M⁺]. Anal. Calcd for C₃₈H₆₄Cl₂O₂P₂Ru: C, 58.01; H, 8.20; Cl, 9.01; Ru, 12.84. Found: C, 58.16; H, 7.99; Cl, 9.10; Ru, 13.10. IR (KBr, cm⁻¹): ν (C=C) 1591 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, toluene, –80 °C): δ 28.0, 2.8 (each d, AB system, $^2J_{\text{PP}} = 358$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl₃, 22 °C): δ 350.2 (t, $^2J_{\text{PC}} = 16.0$ Hz, Ru=C), 132.9–123.4 (m, C–Ph), 109.2 (s, =CHPh), 70.3 (s, OCH₂CH₂), 60.3 (s, OCH₃), 33.7 (m, $^{13}J = 8.3$ Hz, PCH), 29.0–26.3 (m, CH₂ of C₆H₁₁), 20.3 (m, $^{13}J = 9.1$ Hz, PCH₂). ^1H NMR (250.13 MHz, CDCl₃, 22 °C): δ 7.28–6.76 (m, 5 H, C₆H₅), 4.34 (t, $^4J_{\text{PH}} = 3.7$ Hz, 1 H, CHPh), 3.78 (m, 4 H, CH₂OCH₃), 3.39 (s, 6 H, OCH₃), 2.38 (m, 4 H, PCH₂CH₂), 2.11–0.79 (m, 22 H, C₆H₁₁).

Acetonitrile-cis-Dichloro-cis-bis(ether-phosphine)ruthenium(II) Complexes 4a–c. Acetonitrile (48 mg, 1.2 mmol) was added to a solution of **1a–c** (1.0 mmol) in 10 mL of dichloromethane. The mixture was stirred for 30 min in which the color changed from red to yellow. The solvent was removed under reduced pressure and the residue was washed with two portions of *n*-hexane (each 10 mL). The solid was filtered off and dried in vacuo.

Acetonitrile-cis-Dichloro-cis-bis[(methoxyethyl)diphenylphosphine-P;O',P']ruthenium(II) (4a). **4a** was obtained as a yellow powder: yield 90%; mp 169 °C dec. FAB-MS: m/z 666 [M⁺ – Cl]. Anal. Calcd for C₃₂H₃₇Cl₂NO₂P₂Ru: C, 54.78; H, 5.32; N, 2.00; Cl, 10.11; Ru, 14.41. Found: C, 54.63; H, 5.34; N, 2.19; Cl, 10.49; Ru, 14.15. IR (KBr, cm⁻¹): ν (CN) 2276 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 49.6, 47.8 (each d, AB system, $^2J_{\text{PP}} = 36$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl₃, –30 °C): δ 135.6–127.4 (m, C–Ph), 121.1 (s, CH₃CN), 71.8 (s, OCH₂CH₂, P[–]O), 67.7 (s, OCH₂CH₂, P[–]O), 60.9 (s, OCH₃, P[–]O), 57.6 (s, OCH₃, P[–]O), 31.1 (m, PCH₂, P[–]O), 30.7 (m, PCH₂, P[–]O), 3.4 (s, CH₃CN). ^1H NMR (80.13 MHz, CDCl₃,

–30 °C): δ 8.02–6.76 (m, 20 H, C₆H₅), 3.99 (m, 4 H, CH₂OCH₃), 2.93–2.50 (m, 4 H, PCH₂), 2.84 (s, 6 H, OCH₃), 1.45 (s, 3 H, CH₃CN).

Acetonitrile-cis-Dichloro-cis-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P;O',P']ruthenium(II) (4b). **4b** was obtained as a yellow powder in 92% yield, mp 173 °C dec. FAB-MS: m/z 750 [M⁺ – Cl]. Anal. Calcd for C₃₆H₄₁Cl₂NO₄P₂Ru: C, 55.04; H, 5.26; N, 1.78; Cl, 9.03; Ru, 12.86. Found: C, 54.67; H, 5.47; N, 2.04; Cl, 8.82; Ru, 12.50. IR (KBr, cm⁻¹): ν (CN) 2278 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 52.7 (d, $^2J_{\text{PP}} = 37$ Hz, P[–]O), 31.0 (d, $^2J_{\text{PP}} = 37$ Hz, P[–]O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CD₂Cl₂, –30 °C): δ 137.3–124.8 (m, C–Ph), 120.9 (s, CH₃CN), 102.9 (d, $^2J_{\text{PC}} = 28$ Hz, CH₂CH, P[–]O), 99.8 (m, CH₂CH, P[–]O), 68.0 (m, OCH₂CH₂, P[–]O), 67.1 (m, OCH₂CH₂, P[–]O), 37.6 (m, PCH₂, P[–]O), 33.4 (m, PCH₂, P[–]O), 25.5 (s, OCH₂CH₂, P[–]O), 25.0 (s, OCH₂CH₂, P[–]O), 4.2 (s, CH₃CN). ^1H NMR (80.13 MHz, CDCl₃, –30 °C): δ 8.35–6.37 (m, 20 H, C₆H₅), 5.28–5.07 (m, 2 H, CH₂CH), 4.58–0.99 (m, 16 H, alkanes), 1.53 (s, 3 H, CH₃CN).

Acetonitrile-cis-Dichloro-cis-bis[dicyclohexyl(methoxyethyl)phosphine-P;O',P']ruthenium(II) (4c). **4c** was obtained as a green powder in 85% yield, mp 173 °C dec. FAB-MS: m/z 690 [M⁺ – Cl]. Anal. Calcd for C₃₂H₆₁Cl₂NO₂P₂Ru: C, 52.96; H, 8.47; N, 1.93; Cl, 9.77; Ru, 13.93. Found: C, 52.65; H, 8.14; N, 2.01; Cl, 9.43; Ru, 13.60. IR (KBr, cm⁻¹): ν (CN) 2272 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 54.7 (d, $^2J_{\text{PP}} = 27$ Hz, P[–]O), 44.2 (d, $^2J_{\text{PP}} = 27$ Hz, P[–]O). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl₃, –30 °C): δ 125.7 (m, CH₃CN), 67.0 (m, OCH₂CH₂, P[–]O), 66.5 (m, OCH₂CH₂, P[–]O), 60.2 (s, OCH₃, P[–]O), 57.7 (s, OCH₃, P[–]O), 32.3 (m, PCH), 29.0–24.5 (m, CH₂ of C₆H₁₁), 22.5 (m, PCH₂), 4.4 (s, CH₃CN). ^1H NMR (80.13 MHz, CDCl₃, –30 °C): δ 3.80 (m, 2 H, CH₂OCH₃, P[–]O), 3.57 (m, 2 H, CH₂OCH₃, P[–]O), 3.28 (m, 6 H, OCH₃), 2.49 (m, 4 H, PCH₂CH₂), 2.12–0.73 (m, 22 H, C₆H₁₁), 1.41 (s, 3 H, CH₃CN).

trans-Dichloro[dicyclohexyl(methoxyethyl)phosphine-O,P']-[dicyclohexyl(methoxyethyl)phosphonio]dithiocarboxylato-S,S']ruthenium(II) (5c). **1c** (400 mg, 0.58 mmol) was dissolved in 20 mL of toluene and treated with carbon disulfide (91 mg, 1.20 mmol). The mixture was stirred and heated up to 80 °C for 30 min. During that time a color change from deep red to dark purple occurred. The solvent was removed in vacuo and the residue was treated with 1/1 diethyl ether/*n*-pentane (10 mL) to give a dark purple precipitate, which was collected by filtration (G 3), and dried in vacuo: yield 90%; mp 69 °C dec. FAB-MS: m/z 760 [M⁺]. Anal. Calcd for C₃₁H₅₈Cl₂O₂P₂RuS₂: C, 48.94; H, 7.68; Cl, 9.32; S, 8.43; Ru, 13.28. Found: C, 48.30; H, 8.31; Cl, 9.14; S, 8.53; Ru, 13.55. IR (KBr, cm⁻¹): ν (CS) 1006 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, toluene, –30 °C): δ 51.2 (s, P[–]O), 24.5 (s, S₂CP[–]O). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.90 MHz, CDCl₃, 22 °C): δ 211.7 (d, $^1J_{\text{PC}} = 34.5$ Hz, S₂CP[–]O), 69.2 (s, OCH₂CH₂, P[–]O), 65.0 (s, OCH₂CH₂, P[–]O), 59.0 (s, OCH₃, P[–]O), 58.2 (s, OCH₃, P[–]O), 38.1 (m, PCH, P[–]O), 30.9 (d, $^1J_{\text{PC}} = 31.8$ Hz, PCH), 28.7–25.2 (m, CH₂ of C₆H₁₁), 17.8 (m, PCH₂, P[–]O), 17.1 (m, PCH₂, P[–]O).

all-trans-Dicarbonyldichlorobis[dicyclohexyl(methoxyethyl)phosphine-P;O',P']ruthenium(II) (6c). A solution of **1c** (250 mg, 0.36 mmol) in 10 mL of dichloromethane was stirred under an atmosphere of carbon monoxide at ambient temperature for 30 min. During that time a color change from dark red to yellow occurred. The mixture was concentrated to 1 mL and purified by column chromatography on activated silica gel (length of column 20 cm). A yellow fraction was eluted with 1/1 diethyl ether/*n*-pentane and evaporated to dryness. The residue was washed with *n*-pentane (10 mL) and collected by filtration (G 3) to yield 85% of **6c**, mp 81 °C dec. FD-MS: m/z 740 [M⁺]. Anal. Calcd for C₃₂H₅₈Cl₂O₄P₂Ru: C, 51.89; H, 7.89; Cl, 9.57; Ru, 13.64. Found: C, 52.22; H, 7.94; Cl, 10.00; Ru, 13.80. IR (KBr, cm⁻¹): ν (CO) 1981 (vs). $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 19.3 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CDCl₃, –30 °C): δ 199.7 (t, $^2J_{\text{PC}} = 12.6$ Hz, CO), 68.1 (s, OCH₂CH₂), 58.3 (s, OCH₃), 33.6 (m, $^{13}J = 11.4$ Hz, PCH), 27.2–25.7 (m, CH₂ of C₆H₁₁), 21.0 (m, $^{13}J = 11.3$ Hz, PCH₂).

Carbonyl-trans-dichloro-trans-bis[dicyclohexyl(methoxyethyl)phosphine-P;O',P']ruthenium(II) (7c). A slow stream of argon was passed through a solution of **6c** (200 mg, 0.27 mmol) in 10 mL of CH₂Cl₂ at 40 °C. After the mixture was refluxed for 30 min, the solution was cooled to room temperature and evaporated to dryness. The residue was treated with 10 mL of *n*-pentane to give a light yellow

(15) A part of an AXX' spectrum, $J = [^4J_{\text{PH}} + ^4J_{\text{PH}}]$.

precipitate which was filtered off, and dried in vacuo: yield 95% of **7c**; mp 113 °C. FD-MS: m/z 714 [M^+]. Anal. Calcd for $C_{31}H_{58}Cl_2O_3P_2Ru$: C, 52.24; H, 8.20; Cl, 9.95; Ru, 14.18. Found: C, 52.08; H, 8.28; Cl, 10.27; Ru, 13.95. IR (KBr, cm^{-1}): $\nu(CO)$ 1938 (vs). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 47.0, 11.7 (each d, AB system, $^2J_{PP} = 303$ Hz). $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, $-30^\circ C$): δ 205.5 (m, $^{14}J = 13.1$ Hz, CO), 73.5 (m, OCH_2CH_2 , $P^{\sim}O$), 68.4 (m, OCH_2CH_2 , $P^{\sim}O$), 62.5 (s, OCH_3 , $P^{\sim}O$), 58.2 (s, OCH_3 , $P^{\sim}O$), 33.3 (m, PCH, $P^{\sim}O$), 32.3 (m, PCH, $P^{\sim}O$), 28.8–25.8 (m, CH_2 of C_6H_{11}), 22.4 (m, PCH_2 , $P^{\sim}O$), 19.5 (m, PCH_2 , $P^{\sim}O$).

trans-Bis(tert-butyl isocyanide)-cis-dichloro-cis-bis(ether-phosphine)ruthenium(II) Complexes 8a,b. A suspension of **1a,b** (1.00 mmol) in 20 mL of toluene was treated with CN^tBu (175 mg, 2.1 mmol) and refluxed for 1 h. During that time the mixture became a yellow solution. After the solution was cooled to room temperature yellow crystals precipitated, which were collected.

trans-Bis(tert-butyl isocyanide)-cis-dichloro-cis-bis(methoxyethyl)diphenylphosphine-P]ruthenium(II) (8a). **8a** was obtained as bright yellow crystals: yield 80%; mp 248 °C dec. FD-MS: m/z 827 [M^+]. Anal. Calcd for $C_{40}H_{52}Cl_2N_2O_4P_2Ru$: C, 58.11; H, 6.34; N, 3.39; Cl, 8.58; Ru, 12.22. Found: C, 58.00; H, 6.47; N, 3.50; Cl, 9.06; Ru, 12.55. IR (KBr, cm^{-1}): $\nu(CN)$ 2124 (vs). Far-IR (polyethylene, cm^{-1}): $\nu_{as}(RuCl_2)$ 310 (m), $\nu_s(RuCl_2)$ 262 (w). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 12.8 (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, $22^\circ C$): δ 152.1 (m, CN^tBu), 136.7–127.7 (m, C–Ph), 68.6 (s, OCH_2CH_2), 58.1 (s, OCH_3), 56.4 (s, $CNCMe_3$), 30.1 (s, $CNCMe_3$), 27.0 (m, $^{13}J = 12.6$ Hz, PCH_2). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 7.80–7.21 (m, 20 H, C_6H_5), 3.58–3.38 (m, 4 H, CH_2OCH_3), 3.24 (s, 6 H, OCH_3), 3.06–2.33 (m, 4 H, PCH_2), 0.97 [s, 18 H, $C(CH_3)_3$].

trans-Bis(tert-butyl isocyanide)-cis-dichloro-cis-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P]ruthenium(II) (8b). **8b** was obtained as yellow crystals: yield 83%; mp 245 °C dec. FD-MS: m/z 911 [M^+]. Anal. Calcd for $C_{44}H_{56}Cl_2N_2O_4P_2Ru$: C, 58.02; H, 6.20; N, 3.08; Cl, 7.78; Ru, 11.10. Found: C, 58.42; H, 6.23; N, 3.30; Cl, 7.94; Ru, 11.15. IR (KBr, cm^{-1}): $\nu(CN)$ 2125 (vs). Far-IR (polyethylene, cm^{-1}): $\nu_{as}(RuCl_2)$ 313 (m), $\nu_s(RuCl_2)$ 271 (w). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 21.3 (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, $22^\circ C$): δ 153.6 (m, CN^tBu), 134.2–127.0 (m, C–Ph), 100.4 (s, PCH_2CH), 66.5 (s, OCH_2CH_2), 56.4 (s, $CNCMe_3$), 33.6 (m, $^{13}J = 12.3$ Hz, PCH_2), 30.4 (s, $CNCMe_3$), 25.4 (s, OCH_2CH_2). 1H NMR (250.13, $CDCl_3$, $22^\circ C$): δ 7.73–7.24 (m, 20 H, Ph), 4.39 (m, 2 H, CH_2CH), 3.69–0.85 (m, 16 H, alkanes), 1.10 [s, 18 H, $C(CH_3)_3$].

trans-Bis(tert-butyl isocyanide)-cis-dichloro-cis-bis(dicyclohexyl(methoxyethyl)phosphine-P]ruthenium(II) (8c). CN^tBu (125 mg, 1.50 mmol) was added to a solution of **1c** (360 mg, 0.53 mmol) in 15 mL of dichloromethane. The mixture was stirred at ambient temperature for 1 h. During that time the color changed from dark red to light green. The solvent was removed under reduced pressure, and the residue was washed with two portions of *n*-pentane (each 10 mL). The light green precipitate was filtered off and dried in vacuo to yield 95% of **8c**, mp 218 °C dec. FD-MS: m/z 852 [M^+]. Anal. Calcd for $C_{40}H_{76}Cl_2N_2O_2P_2Ru$: C, 56.46; H, 9.00; N, 3.29; Cl, 8.33; Ru, 11.88. Found: C, 56.85; H, 9.37; N, 3.29; Cl, 8.43; Ru, 12.20. IR (KBr, cm^{-1}): $\nu(CN)$ 2101 (vs). Far-IR (polyethylene, cm^{-1}): $\nu_{as}(RuCl_2)$ 306 (m), $\nu_s(RuCl_2)$ 277 (w). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 12.9 (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, $22^\circ C$): δ 155.2 (m, CN^tBu), 69.5 (s, OCH_2CH_2), 58.3 (s, OCH_3), 56.7 (s, $CNCMe_3$), 35.0 (m, $^{13}J = 9.8$ Hz, PCH), 30.6 (s, $CNCMe_3$), 28.6–26.3 (m, CH_2 of C_6H_{11}), 23.8 (m, $^{13}J = 9.4$ Hz, PCH_2). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 3.72 (m, 4 H, CH_2OCH_3), 3.32 (s, 6 H, OCH_3), 2.55–2.18 (m, 4 H, PCH_2), 2.16–1.05 (m, 44 H, C_6H_{11}), 1.52 [s, 18 H, $C(CH_3)_3$].

(tert-Butyl isocyanide)-trans-dichloro-trans-bis(methoxyethyl)diphenylphosphine-P;O',P']ruthenium(II) (9a). **1a** (794 mg, 1.2 mmol) was dissolved in 15 mL of dichloromethane and cooled with an ice bath. CN^tBu (100 mg, 1.2 mmol) dissolved in CH_2Cl_2 (10 mL) was carefully added to the red solution, and the mixture was stirred at 0 °C for 15 min. Instantaneously the color of the solution changed to orange. The mixture was evaporated to dryness, and the residue was stirred with methanol (10 mL) to give a yellow precipitate, which was collected by filtration (G 3), washed with 10 mL of diethyl ether, and dried in vacuo. Crystals were grown from a solution of **9a** in

dichloromethane by slow diffusion of *n*-hexane: yield 72%; mp 213 °C dec. FD-MS: m/z 745 [M^+]. Anal. Calcd for $C_{35}H_{43}Cl_2NO_2P_2Ru$: C, 56.53; H, 5.83; N, 1.88; Cl, 9.53; Ru, 13.59. Found: C, 57.03; H, 6.06; N, 1.96; Cl, 9.86; Ru, 13.40. IR (KBr, cm^{-1}): $\nu(CN)$ 2099 (s), 2086 (s). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 44.3, 15.5 (each d, AB system, $^2J_{PP} = 350$ Hz). $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, $-30^\circ C$): δ 154.8 (m, $^{14}J = 15.4$ Hz, CN^tBu), 133.8–127.5 (m, C–Ph), 73.1 (m, OCH_2CH_2 , $P^{\sim}O$), 66.1 (m, OCH_2CH_2 , $P^{\sim}O$), 60.9 (s, OCH_3 , $P^{\sim}O$), 58.3 (s, OCH_3 , $P^{\sim}O$), 57.0 (s, $CNCMe_3$), 31.3 (s, $CNCMe_3$), 26.7 (m, PCH_2 , $P^{\sim}O$), 24.5 (m, PCH_2 , $P^{\sim}O$). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 7.94–7.37 (m, 20 H, C_6H_5), 3.53–2.89 (m, 4 H, PCH_2), 3.22 (m, 4 H, CH_2OCH_3), 2.58 (s, 6 H, OCH_3), 1.40 [s, 9 H, $C(CH_3)_3$].

(tert-Butyl isocyanide)-trans-dichloro-trans-bis(dicyclohexyl(methoxyethyl)phosphine-P;O',P']ruthenium(II) (9c). A mixture of **1c** (104 mg, 0.15 mmol) and **8c** (128 mg, 0.15 mmol) dissolved in 10 mL of toluene was refluxed for 1 h. The solution was cooled to room temperature and concentrated to 1 mL and was chromatographed on activated silica gel (length of column 20 cm). A yellow fraction was eluted with diethyl ether and evaporated to dryness. The residue was stirred with 10 mL of *n*-pentane to give a yellow precipitate, which was filtered off and dried in vacuo: yield 74% of **9c**; mp 165 °C dec. FD-MS: m/z 767 [M^+]. Anal. Calcd for $C_{35}H_{67}Cl_2NO_2P_2Ru$: C, 54.75; H, 8.80; N, 1.82; Cl, 9.23; Ru, 13.16. Found: C, 54.38; H, 8.58; N, 1.83; Cl, 9.18; Ru, 13.45. IR (KBr, cm^{-1}): $\nu(CN)$ 2091 (s), 2059 (vs). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 43.0, 11.6 (each d, AB system, $^2J_{PP} = 315$ Hz). $^{13}C\{^1H\}$ NMR (20.15 MHz, $CDCl_3$, $-30^\circ C$): δ 156.2 (m, $^{14}J = 14.3$ Hz, CN^tBu), 72.9 (m, OCH_2CH_2 , $P^{\sim}O$), 69.2 (m, OCH_2CH_2 , $P^{\sim}O$), 62.7 (s, OCH_3 , $P^{\sim}O$), 58.3 (s, OCH_3 , $P^{\sim}O$), 56.3 (s, $CNCMe_3$), 34.9 (m, PCH, $P^{\sim}O$), 33.1 (m, PCH, $P^{\sim}O$), 30.9 (s, $CNCMe_3$), 29.6–26.1 (m, CH_2 of C_6H_{11}), 22.8 (m, PCH_2 , $P^{\sim}O$), 18.6 (m, PCH_2 , $P^{\sim}O$). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 3.47 (m, 4 H, CH_2OCH_3), 3.22–3.05 (m, 6 H, OCH_3), 1.99–0.95 (m, 48 H, alkanes), 1.09 [s, 9 H, $C(CH_3)_3$].

(tert-Butyl isocyanide)-cis-dichloro-cis-bis(ether-phosphine)ruthenium(II) Complexes 10a,b. A suspension of **1a,b** (0.44 mmol) and **8a,b** (0.44 mmol) in 10 mL of toluene was heated to reflux for 1 h. During that time the suspension dissolved, and the color changed from red to light orange. The solution was cooled to room temperature to yield yellow crystals, which were collected, washed with 10 mL of *n*-pentane, and dried in vacuo.

(tert-Butyl isocyanide)-cis-dichloro-cis-bis(methoxyethyl)diphenylphosphine-P;O',P']ruthenium(II) (10a). **10a** was obtained as bright yellow crystals in 72% yield, mp 193 °C dec. FAB-MS: m/z 708 [$M^+ - Cl$]. Anal. Calcd for $C_{35}H_{43}Cl_2NO_2P_2Ru$: C, 56.53; H, 5.83; N, 1.88; Cl, 9.53; Ru, 13.59. Found: C, 56.63; H, 6.03; N, 1.93; Cl, 9.67; Ru, 13.30. IR (KBr, cm^{-1}): $\nu(CN)$ 2121 (vs). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 49.2, 42.0 (each d, AB system, $^2J_{PP} = 33.5$ Hz). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, $22^\circ C$): δ 155.3 (m, $^{14}J = 16.2$ Hz, CN^tBu), 133.6–125.2 (m, C–Ph), 72.0 (m, OCH_2CH_2 , $P^{\sim}O$), 68.2 (m, OCH_2CH_2 , $P^{\sim}O$), 61.6 (s, OCH_3 , $P^{\sim}O$), 58.2 (s, OCH_3 , $P^{\sim}O$), 56.8 (s, $CNCMe_3$), 32.2 (m, PCH_2 , $P^{\sim}O$), 30.7 (s, $CNCMe_3$), 21.4 (m, PCH_2 , $P^{\sim}O$). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 7.89–6.75 (m, 20 H, C_6H_5), 3.89 (m, 4 H, CH_2OCH_3), 2.98–2.45 (m, 4 H, PCH_2), 2.86 (s, 6 H, OCH_3), 0.92 [s, 9 H, $C(CH_3)_3$].

(tert-Butyl isocyanide)-cis-dichloro-cis-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P;O',P']ruthenium(II) (10b). **10b** was obtained as yellow crystals in 69% yield, mp 238 °C dec. FAB-MS: m/z 792 [$M^+ - Cl$]. Anal. Calcd for $C_{39}H_{47}Cl_2NO_4P_2Ru$: C, 56.59; H, 5.72; N, 1.69; Cl, 8.57; Ru, 12.21. Found: C, 56.49; H, 6.05; N, 1.81; Cl, 8.59; Ru, 12.45. IR (KBr, cm^{-1}): $\nu(CN)$ 2111 (vs). Far-IR (polyethylene, cm^{-1}): $\nu_{as}(RuCl_2)$ 309 (w), $\nu_s(RuCl_2)$ 276 (m). $^1P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2 , $-30^\circ C$): δ 47.1 (d, $^2J_{PP} = 34.6$ Hz, $P^{\sim}O$), 34.5 (d, $^2J_{PP} = 34.6$ Hz, $P^{\sim}O$). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, $22^\circ C$): δ 156.3 (m, $^{14}J = 20.3$ Hz, CN^tBu), 135.4–127.0 (m, C–Ph), 103.5 (m, PCH_2CH , $P^{\sim}O$), 99.9 (m, PCH_2CH , $P^{\sim}O$), 68.1 (m, OCH_2CH_2 , $P^{\sim}O$), 66.3 (s, OCH_2CH_2 , $P^{\sim}O$), 57.0 (s, $CNCMe_3$), 38.7 (m, PCH_2 , $P^{\sim}O$), 35.5 (m, PCH_2 , $P^{\sim}O$), 30.6 (s, $CNCMe_3$), 25.8 (s, OCH_2CH_2 , $P^{\sim}O$), 25.2 (s, OCH_2CH_2 , $P^{\sim}O$). 1H NMR (80.13 MHz, $CDCl_3$, $-30^\circ C$): δ 8.22–6.60 (m, 20 H, C_6H_5), 5.15–4.20 (m, 2 H, CH_2CH), 3.78–0.83 (m, 16 H, alkanes), 1.01 [s, 9 H, $C(CH_3)_3$].

(tert-Butyl isocyanide)carbonyl-trans-dichloro-trans-bis(methoxyethyl)diphenylphosphine-P]ruthenium(II) (11a). Method a. Car-

Table 1. Crystal Data and Refinement Details for Compounds **2a**, **3a**, **3c**, **9a**, and **10b**

	2a ·CH ₂ Cl ₂	3a	3c	9a	10b
formula	C ₃₁ H ₃₆ Cl ₄ O ₄ P ₂ RuS	C ₃₈ H ₄₀ Cl ₂ O ₂ P ₂ Ru	C ₃₈ H ₆₄ Cl ₂ O ₂ P ₂ Ru	C ₃₅ H ₄₃ Cl ₂ NO ₂ P ₂ Ru	C ₃₉ H ₄₇ Cl ₂ NO ₄ P ₂ Ru
fw	809.5	762.6	786.8	743.6	827.7
color and habit	yellow needles	red cubes	red plates	orange cubes	yellow cubes
cryst dimens	0.1 × 0.25 × 0.25	0.4 × 0.25 × 0.1	0.1 × 0.2 × 0.5	0.25 × 0.25 × 0.35	0.1 × 0.25 × 0.25
cryst syst	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	P2 ₁ /c	P1	P1	P1	P2 ₁ /c
a, Å	18.991(7)	9.687(1)	12.420(2)	9.416(2)	9.870(3)
b, Å	9.717(3)	11.768(2)	12.621(2)	12.791(2)	11.171(4)
c, Å	19.930(6)	16.386(2)	13.556(2)	15.665(4)	34.778(14)
α, deg	90	103.08(1)	91.66(3)	79.39(2)	90
β, deg	110.94(3)	103.84(1)	101.34(3)	76.59(2)	93.27(4)
γ, deg	90	91.37(1)	110.11(3)	78.43(1)	90
V, Å ³	3435(2)	1760.6(4)	1945.6(6)	1779.1(7)	3828(2)
Z	4	2	2	2	4
d _{calcd} , g cm ⁻³	1.565	1.439	1.343	1.388	1.436
2θ limits, deg	4–50	4–50	4–50	4–50	4–50
T, °C	–100	–100	–100	–100	–100
μ(Mo Kα), mm ⁻¹	0.960	0.721	0.654	0.712	0.673
no. of reflns measd	20603	12388	13694	10956	26202
no. of unique data with I ≥ 2σ(I)	3963	5354	5709	5530	4217
no. of variables	400	407	406	389	443
S	1.289	1.453	1.02	0.962	1.144
R1 ^a	0.0378	0.0214	0.0331	0.0228	0.027
wR2 ^b	0.0865	0.0515	0.0395 ^c	0.0583	0.0526

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)]^{0.5}$. ^c R_w = $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{0.5}$.

bon monoxide was passed through a solution of **9a** (142 mg, 0.19 mmol) in 10 mL of dichloromethane at 0 °C. The mixture was stirred under a CO atmosphere for 5 min. The solvent was removed under reduced pressure, and the residue was washed with 10 mL of diethyl ether to yield a light yellow precipitate, which was collected by filtration (G 3), and dried in vacuo: yield 95% of **11a**; mp 173 °C. FD-MS: *m/z* 772 [M⁺].

Method b. CO was bubbled through a solution of **10a** (187 mg, 0.25 mmol) in 10 mL of dichloromethane at ambient temperature. An immediate color change from orange to light yellow occurred. Stirring was maintained under a CO atmosphere for 10 min. The mixture was evaporated to dryness, and the residue was stirred with 10 mL of diethyl ether to give a yellow precipitate, which was filtered off, and dried in vacuo to yield 90% of **11a**, mp 172 °C. FD-MS: *m/z* 772 [M⁺]. Anal. Calcd for C₃₆H₄₃Cl₂NO₃P₂Ru: C, 56.03; H, 5.62; N, 1.82; Cl, 9.19; Ru, 13.10. Found: C, 56.54; H, 6.07; N, 1.96; Cl, 9.44; Ru, 13.50. IR (KBr, cm⁻¹): ν(CN) 2168 (s), ν(CO) 2014 (vs). Far-IR (polyethylene, cm⁻¹): ν_{as}(RuCl₂) 320 (m). ³¹P{¹H} NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 12.2 (s). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂, 22 °C): δ 201.4 (t, ²J_{PC} = 12.1 Hz, CO), 147.3 (m, CN^tBu), 136.1 (m, *ipso*-C of C₆H₅), 134.8–129.7 (m, C–Ph), 69.6 (s, OCH₂CH₂), 59.7 (s, OCH₃), 59.3 (s, CNCMe₃), 31.2 (s, CNCMe₃), 28.5 (m, ¹³J = 13.5 Hz, PCH₂). ¹H NMR (80.13 MHz, CDCl₃, –30 °C): δ 7.74–7.38 (m, 20 H, C₆H₅), 3.36 (m, 4 H, CH₂OCH₃), 3.19 (s, 6 H, OCH₃), 3.03 (m, 4 H, PCH₂), 1.08 [s, 9 H, C(CH₃)₃].

(*tert*-Butyl isocyanide)carbonyl-*trans*-dichloro-*trans*-bis[dicyclohexyl(methoxyethyl)phosphine-P]ruthenium(II) (**11c**). **9c** (154 mg, 0.20 mmol) was dissolved in 15 mL of dichloromethane and stirred under a CO pressure of 1 bar at 40 °C. Stirring was maintained for 1 h, and after the solution was cooled to room temperature the solvent was removed under reduced pressure. The yellow residue was extracted with two portions of *n*-pentane (each 10 mL), and the two extracts were collected and concentrated to 1 mL. The solution was chromatographed on activated silica gel (length of column 20 cm). A yellow fraction was eluted with 1/1 diethyl ether/*n*-pentane, which was evaporated to dryness to give a yellow powder of **11c**: yield 65%, mp 134 °C. FD-MS: *m/z* 795 [M⁺]. Anal. Calcd for C₃₆H₆₇Cl₂NO₃P₂Ru: C, 54.33; H, 8.49; N, 1.76; Cl, 8.91; Ru, 12.70. Found: C, 54.11; H, 8.60; N, 1.99; Cl, 9.09; Ru, 12.50. IR (KBr, cm⁻¹): ν(CN) 2178 (s), ν(CO) 1966 (vs). ³¹P{¹H} NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 17.6 (s). ¹³C{¹H} NMR (62.90 MHz, CDCl₃, 22 °C): δ 204.2 (t, ²J_{PC} = 12.3 Hz, CO), 148.8 (m, CN^tBu), 68.9 (s, OCH₂CH₂), 58.2 (s, OCH₃), 57.8 (s, CNCMe₃), 34.3 (m, ¹³J = 10.8 Hz, PCH₂), 30.0 (s, CNCMe₃), 28.0–26.2 (m, CH₂ of C₆H₁₁), 22.2 (m, ¹³J = 9.6 Hz, PCH₂). ¹H NMR (80.13 MHz, CDCl₃, –30 °C): δ 3.68 (m, 4 H, CH₂OCH₃),

3.32 (s, 6 H, OCH₃), 2.58–2.20 (m, 4 H, PCH₂), 2.18–1.19 (m, 44 H, C₆H₁₁), 1.56 [s, 18 H, C(CH₃)₃].

(*tert*-Butyl isocyanide)carbonyl-*cis*-dichloro-*cis*-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P]ruthenium(II) (**12b**). Carbon monoxide was passed through a solution of **10b** (124 mg, 0.15 mmol) in 15 mL of dichloromethane at room temperature for 15 min. During that time the color of the yellow solution changed to almost colorless. The solvent was removed in vacuo to give a white residue, which was washed with two portions of diethyl ether (each 10 mL), and collected by filtration (G 3): yield 92% of **12b**; mp 255 °C dec. FD-MS: *m/z* 856 [M⁺]. Anal. Calcd for C₄₀H₄₇Cl₂NO₃P₂Ru: C, 56.14; H, 5.54; N, 1.64; Cl, 8.29; Ru, 11.81. Found: C, 56.62; H, 5.88; N, 1.76; Cl, 8.74; Ru, 12.05. IR (KBr, cm⁻¹): ν(CN) 2163 (s), ν(CO) 1988 (vs). Far-IR (polyethylene, cm⁻¹): ν_{as}(RuCl₂) 312 (w), ν_s(RuCl₂) 280 (w). ³¹P{¹H} NMR (32.39 MHz, CH₂Cl₂, –30 °C): δ 14.6 (s). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂, 22 °C): δ 196.2 (t, ²J_{PC} = 11.6 Hz, CO), 143.3 (m, CN^tBu), 134.8–128.0 (m, C–Ph), 100.1 (s, PCH₂CH), 67.0 (s, OCH₂CH₂), 58.1 (s, CNCMe₃), 30.5 (m, PCH₂), 30.3 (s, CNCMe₃), 25.8 (s, OCH₂CH₂). ¹H NMR (80.13 MHz, CDCl₃, –30 °C): δ 8.03–7.34 (m, 20 H, C₆H₅), 4.21 (m, 4 H, CH₂CH), 3.65–3.30 (m, 8 H, OCH₂), 1.95–1.85 (m, 4 H, PCH₂), 1.12–0.96 (m, 4 H, CH₂CH₂), 0.82 [s, 9 H, C(CH₃)₃].

Crystallographic Analyses. Single crystals of **2a** and **3a** were obtained by slow diffusion of diethyl ether into solutions of **2a** and **3a** in dichloromethane, respectively; in the case of **2a** both solvents were saturated with SO₂. The asymmetric unit of **2a** contains one disordered molecule of CH₂Cl₂. Single crystals of **3c** were grown from concentrated diethyl ether solutions of **3c**. Single crystals of **9a** and **10b** were obtained by slow diffusion of *n*-hexane into solutions of **9a** and **10b** in dichloromethane, respectively. All crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters for **2a**, **3a**, **3c**, **9a**, and **10b** are summarized in Table 1. Intensities were collected with the ω-scan technique with scan speed varying from 8 to 30°/min in ω. Scan ranges for **2a**, **3a**, **3c**, **9a**, and **10b**, were 1.2, 1.0, 1.3, 1.0, and 1.2°, respectively. An absorption correction was applied (Ψ-scan, maximum and minimum transmission: **2a**, 0.573, 0.489; **3a**, 0.513, 0.417; **3c**, 0.620, 0.516; **9a**, 0.652, 0.579; **10b**, 0.524, 0.477). All structures were solved by Patterson methods¹⁶ and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). The use of a split model in

Table 2. Selected Interatomic Distances (pm) and Angles (deg) for **2a**, **3a**, **3c**, **9a**, and **10b**

bond lengths		bond angles	
Compound 2a			
Ru(1)–P(1)	230.7(13)	Cl(2)–Ru–S	172.4(5)
Ru(1)–P(2)	235.7(12)	S(1)–Ru–O(4)	91.1(9)
Ru(1)–S(1)	211.9(12)	O(2)–S–Ru	119.1(2)
Ru(1)–O(4)	227.4(3)	Cl(1)–Ru–P(2)	165.7(4)
Compound 3a			
Ru–C(1)	181.5(2)	Ru–C(1)–C(2)	178.6(14)
Ru–O(2)	227.7(13)	C(1)–Ru–Cl(1)	176.0(5)
C(1)–C(2)	131.9(3)	O(2)–Ru–P(1)	178.2(3)
Ru–P(1)	228.4(6)	Cl(2)–Ru–P(2)	160.9(2)
Ru–P(2)	235.1(5)	C(1)–C(2)–C(7)	125.7(2)
Compound 3c			
Ru–C(1)	178.0(3)	P(1)–Ru–P(2)	179.1(1)
Ru–P(1)	238.0(1)	Ru–C(1)–C(2)	178.0(2)
Ru–O(1)	241.1(2)	Cl(1)–Ru–P(2)	90.4(1)
Ru–P(2)	243.9(1)	O(1)–Ru–C(1)	172.6(1)
Compound 9a			
Ru–C(31)	186.8(2)	P(1)–Ru–P(2)	172.9(2)
Ru–O(2)	224.8(14)	N–C(31)–Ru	177.0(2)
C(31)–N(1)	116.6(3)	C(31)–Ru–Cl(1)	93.8(6)
Ru–P(1)	236.4(6)	C(31)–Ru–O(2)	174.5(6)
Compound 10b			
Ru–C(35)	191.8(3)	P(1)–Ru–P(2)	100.7(3)
C(35)–N(1)	115.7(4)	P(1)–Ru–O(2)	177.3(6)
Ru–O(2)	229.1(2)	N–C(35)–Ru	175.4(3)
Ru–P(1)	226.1(11)	C(35)–Ru–Cl(1)	170.6(9)

structure **2a** was necessary to solve the problem of the disordered C27 atom (occupation factor 0.5). Maximum and minimum peaks in the final difference synthesis were 1.27 and –1.09 (**2a**), 0.34 and –0.38 (**3a**), 1.19 and –0.47 (**3c**), 0.40 and –0.36 (**9a**), and 0.29 and –0.36 e Å^{–3} (**10b**), respectively. Selected final atomic coordinates are collected in Table 3.

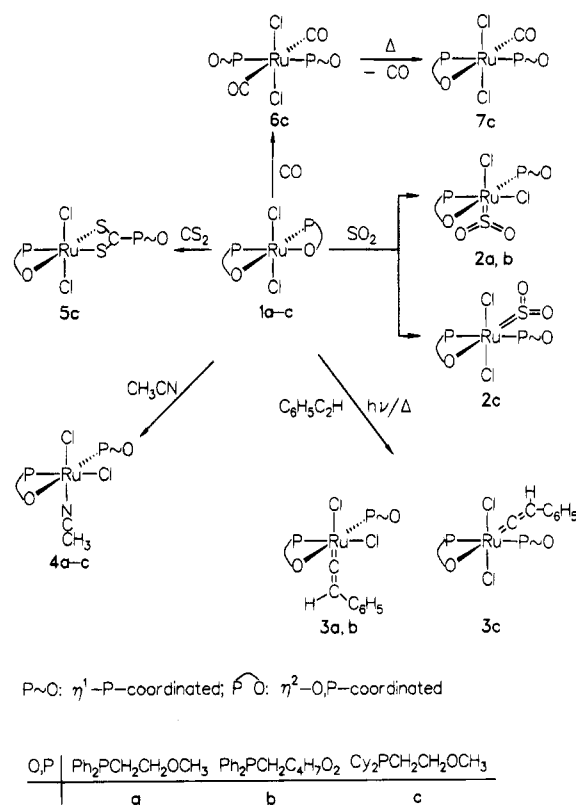
Results and Discussion

There are well-known ruthenium(II) complexes set up with two or three ether–phosphines^{4,17} weakly protecting the metal center by intramolecular chelation incorporating the ether moiety. The resulting mono- or bis(chelates), respectively, represent unsaturated ruthenium(II) fragments containing potentially empty coordination sites. In contrast to the dynamic processes in complexes such as *trans*-Cl₂Ru(CO)(P[–]O)(P[–]O),⁴ in which the ether functions compete for a common coordination site, fluxional behavior does not arise in the bis(chelate) complexes *trans*-Cl₂Ru(P[–]O)₂.^{4,17a}

We therefore are interested in the course of reaction of bis-(η²(O,P)-ether–phosphine)ruthenium(II) complexes toward a variety of small molecules. The ease of Ru–O bond rupture depends on the O basicity, the donor strength of the phosphine, and the coordination abilities of incoming substrates. The employed ether–phosphines comprise a selection of ligands considering different oxygen and phosphorus basicity.

The hitherto not yet described complex *trans*-Cl₂Ru(P[–]O)₂ (**1c**) has been prepared according to the literature¹¹ by ligand substitution starting from Cl₂Ru(PPh₃)₃ and 2 equiv of Cy₂PCH₂CH₂OCH₃. Due to two equivalent phosphorus atoms in the downfield region of the ³¹P{¹H} NMR spectrum of **1c**, a single phosphorus resonance appears at 62.2 ppm. We propose that both ether–phosphines are in *cis*-position analogous to the established structure of the similar bis(chelate) complex **1a**.¹⁸

Scheme 1



Two signals at 72.3 and 62.0 ppm in the ¹³C{¹H} NMR spectrum of **1c** are assigned to the ether oxygen adjacent carbon atoms.

Reactions of 1a–c with Sulfur Dioxide. The reactivity of the complexes **1a–c** toward SO₂ is rather different. If sulfur dioxide is passed through a solution of **1a** in dichloromethane at ambient temperature an instantaneous color change from red to orange occurs (Scheme 1). However refluxing THF is necessary to obtain the related SO₂ complex **2b** by bubbling sulfur dioxide into a solution of the starting compound **1b** (Scheme 1). Both air-stable and orange compounds are obtained in nearly quantitative yields which are easily soluble in chlorinated solvents but rather insoluble in nonpolar solvents. Owing to a chelated O,P ligand and an open-chain ether–phosphine the ³¹P{¹H} NMR spectrum of **2a** is comparable to that of **2b**, both showing an AB pattern. The low coupling constants (**2a**, ²J_{PP} = 27 Hz; **2b**, ²J_{PP} = 28 Hz) are in favor of a *cis*-geometry of the phosphines. The dynamic behavior in solution was investigated with the most stable compound **2a** by variable-temperature ³¹P NMR spectroscopy. Whereas the ³¹P{¹H} NMR spectrum of **2a** displays an AB pattern at ambient temperature, only one signal is observed at considerably higher temperatures. As the temperature is raised, the two doublets first broaden and then coalesce at ca. 353 K from which a ΔG₃₅₃[‡] value of 69.8 kJ mol^{–1} can be calculated.¹⁹ At this temperature **2a** decomposes in solution. This relatively high exchange barrier is due to the rearrangement of the ligands in the coordination sphere of the central atom,¹¹ which requires additional energy compared to the simple “opening and closing” mechanism³ of similar complexes in which the oxygen atom is *cis* to the nonchelating phosphine. The ¹³C{¹H} NMR spectrum of **2a** reveals two sets of signals at δ 71.5 and 67.5 and at δ 61.2 and 58.2 arising from the methylene group and the methyl groups, respectively, which are in the vicinity of the ether

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Table 3. Atomic Coordinates ($\times 10^4$, Esd's in Parentheses) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$)^a for Important Atoms of **2a**, **3a**, **3c**, **9a**, and **10b**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Compound 2a									
Ru(1)	2384(1)	1856(1)	690(1)	20(1)	C(6)	1820(3)	4125(4)	1797(2)	23(1)
S(1)	1310(1)	2402(1)	-59(1)	27(1)	C(12)	1247(3)	1443(4)	1790(2)	27(1)
Cl(1)	2115(1)	-553(1)	775(1)	37(1)	C(18)	3484(2)	5098(4)	1224(2)	27(1)
Cl(2)	3652(1)	1223(1)	1401(1)	27(1)	C(24)	2212(2)	5178(4)	-100(2)	24(1)
P(1)	2052(1)	2334(1)	1672(1)	21(1)	C(25)	2817(2)	1958(4)	2528(2)	25(1)
P(2)	2885(1)	3987(1)	511(1)	21(1)	C(28)	3487(3)	3394(5)	30(2)	31(1)
O(1)	652(2)	2715(4)	99(2)	42(1)	C(29)	3074(3)	2366(5)	-539(3)	40(1)
O(2)	1205(2)	2479(4)	-810(2)	42(1)	C(30)	2423(4)	218(6)	-733(3)	57(2)
O(4)	2792(2)	1267(3)	-214(2)	35(1)					
Compound 3a									
Ru(1)	1065(1)	3616(1)	3092(1)	16(1)	C(14)	1750(2)	1294(2)	1515(1)	23(1)
Cl(1)	-1379(1)	3083(1)	3205(1)	25(1)	C(20)	1044(2)	3264(2)	885(1)	23(1)
Cl(2)	19(1)	5291(1)	2648(1)	25(1)	C(21)	-1170(2)	1888(2)	1212(1)	23(1)
P(2)	1696(1)	2198(1)	3891(1)	17(1)	C(29)	3572(2)	1919(2)	4209(1)	20(1)
P(1)	670(1)	2539(1)	1698(1)	18(1)	C(35)	823(2)	720(2)	3647(1)	21(1)
O(2)	1447(1)	4743(1)	4465(1)	22(1)	C(36)	1279(2)	2947(2)	4903(1)	24(1)
C(1)	2892(2)	3978(1)	3082(1)	19(1)	C(37)	1939(2)	4192(2)	5175(1)	28(1)
C(2)	4220(2)	4265(2)	3088(1)	24(1)	C(38)	2208(2)	5880(2)	4656(1)	29(1)
C(7)	4719(2)	5314(2)	2850(1)	22(1)					
Compound 3c									
Ru(1)	1543(1)	3911(1)	2401(1)	19(1)	C(19)	3619(3)	7336(3)	2287(3)	32(1)
P(1)	1442(1)	5761(1)	2429(1)	22(1)	C(20)	2347(3)	6770(3)	1684(2)	28(1)
P(2)	1613(1)	2003(1)	2363(1)	23(1)	C(21)	-112(3)	5496(3)	1832(3)	33(1)
Cl(2)	930(1)	3715(1)	3961(1)	27(1)	C(22)	-676(3)	4396(3)	1151(2)	32(1)
Cl(1)	1639(1)	3961(1)	653(1)	27(1)	C(23)	-1419(3)	3009(3)	2227(3)	39(1)
O(1)	-516(2)	3464(2)	1677(2)	28(1)	C(29)	282(3)	737(3)	2350(3)	37(1)
C(1)	3086(3)	4427(2)	2909(2)	21(1)	C(35)	2789(3)	1854(3)	3367(2)	29(1)
C(2)	4230(3)	4789(2)	3313(2)	25(1)	C(36)	2012(3)	1610(3)	1196(3)	33(1)
C(8)	5205(3)	5179(2)	2793(2)	26(1)					
Compound 9a									
Ru(1)	2022(1)	1410(1)	2912(1)	16(1)	C(21)	3457(2)	-967(2)	1917(1)	20(1)
P(2)	2159(1)	-410(1)	2851(1)	17(1)	C(27)	566(2)	-1040(2)	2893(1)	22(1)
P(1)	2046(1)	3190(1)	3119(1)	20(1)	C(28)	2854(2)	-1050(2)	3857(1)	23(1)
Cl(2)	-367(1)	1431(1)	3894(1)	25(1)	C(29)	3851(2)	-355(2)	4042(1)	25(1)
Cl(1)	4510(1)	1323(1)	2044(1)	23(1)	C(30)	2313(3)	885(2)	4986(1)	31(1)
O(2)	3075(2)	734(1)	4090(1)	22(1)	C(31)	1145(2)	1834(2)	1921(1)	21(1)
N(1)	598(2)	2052(1)	1302(1)	28(1)	C(32)	-338(3)	2360(2)	650(1)	31(1)
C(6)	2739(2)	4171(2)	2182(1)	24(1)	C(33)	-1946(3)	2503(2)	1154(2)	49(1)
C(12)	3165(2)	3289(2)	3901(1)	24(1)	C(34)	-19(4)	1465(2)	81(2)	54(1)
C(13)	219(2)	3972(2)	3520(1)	27(1)	C(35)	63(3)	3406(2)	94(2)	48(1)
Compound 10b									
Ru(1)	2937(1)	7501(1)	4038(1)	15(1)	C(23)	-334(3)	6309(3)	3787(1)	19(1)
P(2)	624(1)	7603(1)	3979(1)	16(1)	C(29)	-454(3)	8859(3)	3805(1)	19(1)
P(1)	3386(1)	6691(1)	3463(1)	16(1)	C(30)	252(3)	7650(3)	4495(1)	21(1)
Cl(2)	5344(1)	7298(1)	4244(1)	24(1)	C(31)	1151(3)	8578(3)	4695(1)	22(1)
Cl(1)	3488(1)	9532(1)	3833(1)	24(1)	C(32)	1744(4)	9418(3)	5300(1)	34(1)
N(1)	2610(3)	5062(2)	4431(1)	24(1)	C(33)	3228(3)	9129(3)	5252(1)	35(1)
O(1)	907(2)	8563(2)	5087(1)	29(1)	C(34)	3483(3)	9098(3)	4826(1)	31(1)
O(2)	2543(2)	8250(2)	4635(1)	22(1)	C(35)	2716(3)	5958(2)	4269(1)	19(1)
C(6)	2203(3)	6951(3)	3046(1)	22(1)	C(36)	2679(3)	4101(3)	4718(1)	28(1)
C(12)	3598(3)	5069(2)	3499(1)	20(1)	C(37)	1657(4)	3125(3)	4593(1)	47(1)
C(13)	4959(3)	7283(2)	3274(1)	20(1)	C(38)	4117(4)	3604(4)	4730(1)	48(1)
C(14)	5162(3)	7064(3)	2853(1)	23(1)	C(39)	2342(4)	4656(3)	5102(1)	37(1)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

oxygen atoms. The corresponding low field ¹³C resonances are traced back to the chelated phosphine. The ¹³C{¹H} NMR spectrum of **2b** is similar to that of **2a** displaying two sets of resonances which indicate an η^2 -chelated and an η^1 -coordinated ether-phosphine. Both SO₂ stretching frequencies at 1289 and 1123 cm⁻¹ for **2a** and at 1297 and 1125 cm⁻¹ for **2b** are in agreement with an η^1 -coplanar coordination of the sulfur dioxide ligand.²⁰ Complexes **2a** and **2b** are inert toward molecular oxygen in order to form a sulfate compound. This is a further proof for the mentioned bonding mode of the SO₂ ligand, acting as a Lewis base.²⁰ For a full characterization of the structure of **2a**, an X-ray structural analysis has been performed. The

ORTEP drawing of **2a** is shown in Figure 1. Table 2 contains selected bond distances and angles. The central atom is octahedrally coordinated containing *cis*-chlorines and *cis*-phosphines. The SO₂ ligand is *trans*-positioned with respect to chlorine and the η^1 -coplanar arrangement is corroborated. In agreement with the spectroscopic deduced Ru-SO₂ geometry the ruthenium-sulfur distance (211.9(12) pm) was found to be in the range of reported values.²⁰ Thus the spectroscopic data suggest the same coordination geometry for **2b** as it was found for **2a**.

Compared to the reaction of **1a,b** with SO₂ the ruthenium-oxygen bond in **1c** is more readily cleaved by suspending **1c** in liquid sulfur dioxide at -15 °C (Scheme 1). A color change from purple to red indicates the complete conversion of the bis-

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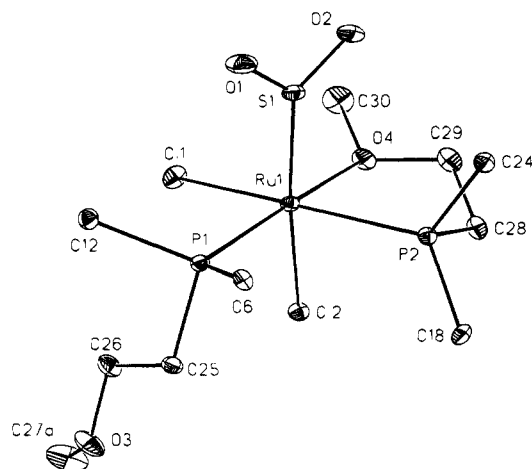


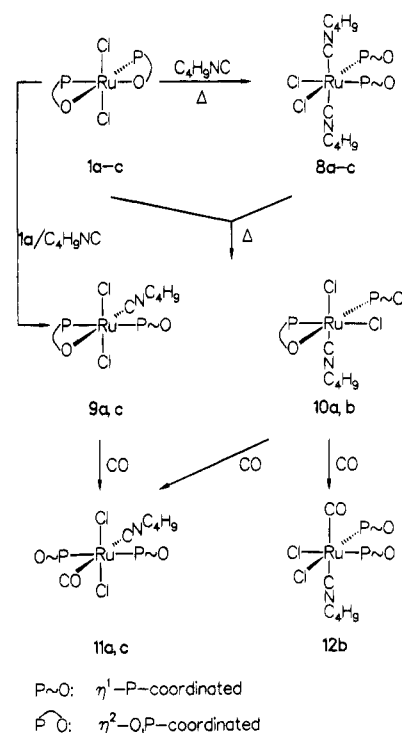
Figure 1. ORTEP plot of the molecular structure of compound **2a**. The phenyl groups are omitted for clarity.

(chelate) **1c** to the SO_2 complex **2c** which is isolated in 90% yield as an orange solid. Marked loss of SO_2 takes place at room temperature. Due to a chelated (downfield doublet) and an open-chain (doublet at higher field) ether-phosphine the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2c** displays an AB pattern at 50.5 and 29.2 ppm (each d, $^2J_{\text{PP}} = 288$ Hz). The large coupling constants indicate a *trans*-arrangement of the phosphines. This configuration is more favorable for sterically demanding phosphines.²¹ In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2c** two sets of resonances account for the two different ether oxygen adjacent carbon atoms. Similar SO_2 stretching frequencies in the IR spectrum of **2c** plead for the same η^1 -coplanar geometry as it was found in **2a,b**.

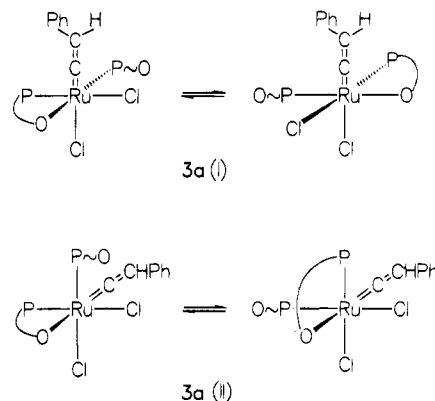
Activation of Phenylacetylene with 1a–c. A variety of η^1 -vinylidene complexes is known containing the CpRuL_2 (L = tertiary phosphine) moiety,²² generated from in situ chlorine abstraction at the ruthenium center and subsequent 1-alkyne to vinylidene tautomerization. However, there are only few examples of ruthenium(II) complexes without cyclopentadienyl containing the $=\text{C}=\text{CHR}$ unit.²³ In most of the cases the rearrangement leads directly to the thermodynamically most stable η^1 -vinylidene species,²⁴ without observation of the η^2 -alkyne intermediate.

Whereas treatment of **1a** with phenylacetylene in dichloromethane at elevated temperatures (40 °C) results in a nearly quantitative formation of the η^1 -vinylidene complex **3a**, refluxing toluene is necessary to produce **3b** from the starting complex **1b** and phenylacetylene (Scheme 1). We found no indication for the occurrence of the metastable η^2 -alkyne compound.^{22b} Both complexes **3a** and **3b** are orange-brown, moderately air-stable compounds, which are readily soluble in chlorinated solvents but insoluble in nonpolar solvents. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a** at –30 °C in CDCl_3 reveals a characteristic resonance at 356.7 ppm (m,¹⁴ $J = 17.7$ Hz) assigned to the highly deshielded C_α and a singlet at 111.9 ppm attributed to the vinylic C_β , which are in the expected range for complexes of this type.^{22b} Strong absorptions at 1592 and 1593 cm^{-1} in

Scheme 2



Scheme 3



the IR spectrum of **3a** and **3b**, respectively, are assigned to the $\text{C}=\text{C}$ stretching mode. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3a,b** are temperature dependent caused from dynamic rearrangements in the coordination sphere of ruthenium. The ^1H NMR spectrum of **3a** at –19 °C reveals a multiplet ($\delta_{\text{H}} = 5.32$ ppm, $J = 1.0$ Hz¹⁵) for the vinylic proton at C_β for isomer I, as for isomer II ($\delta_{\text{H}} = 5.19$ ppm, $J = 3.3$ Hz¹⁵) (Scheme 3).

For satisfactory structural characterization of the vinylidene complexes **3a, b**, we performed an X-ray structural analysis with the example of **3a**. The ORTEP plot of **3a** is shown in Figure 2. Table 2 contains selected bond distances and angles of **3a**. The proposed structure was evidenced to have *cis*-chlorines, *cis*-phosphines, and the η^1 -vinylidene unit *trans* to chlorine. The ruthenium–oxygen distance is 227.7(13) pm, and hence closely related to comparable CO complexes.^{11,18} While the $\text{C}(1)–\text{C}(2)$ distance (131.9(3) pm) is in the region of $\text{C}=\text{C}$ double bonds, the $\text{Ru}–\text{C}(1)$ bond length (181.5(2) pm) is in agreement with reported values.^{22b} Due to the sterically demanding phenyl group at the vinylic β -carbon the bond angle $\text{Cl}(2)–\text{Ru}–\text{P}(2)$ (160.9(2)°) is distorted.

From temperature dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra which have been measured with the example of **3a** in dichloromethane- d_2 a nonrigid structure for **3a, b** in solution is derived (Scheme 3 and Figure 3). If **3a** is dissolved in CD_2Cl_2 two isomers I

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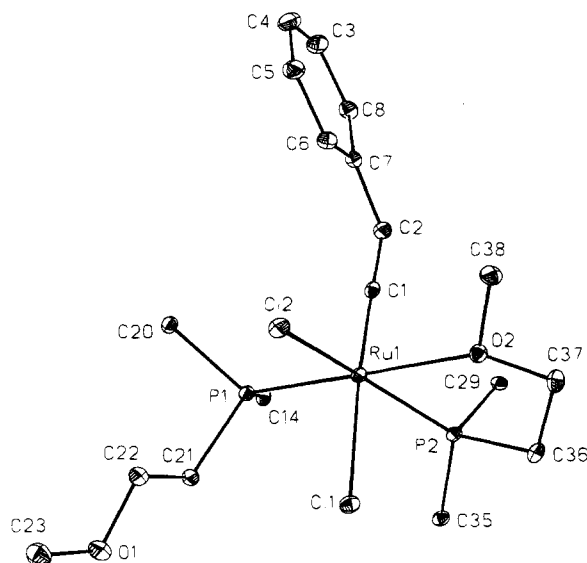


Figure 2. ORTEP presentation of the molecular structure of compound **3a**. The phenyl groups are omitted for clarity.

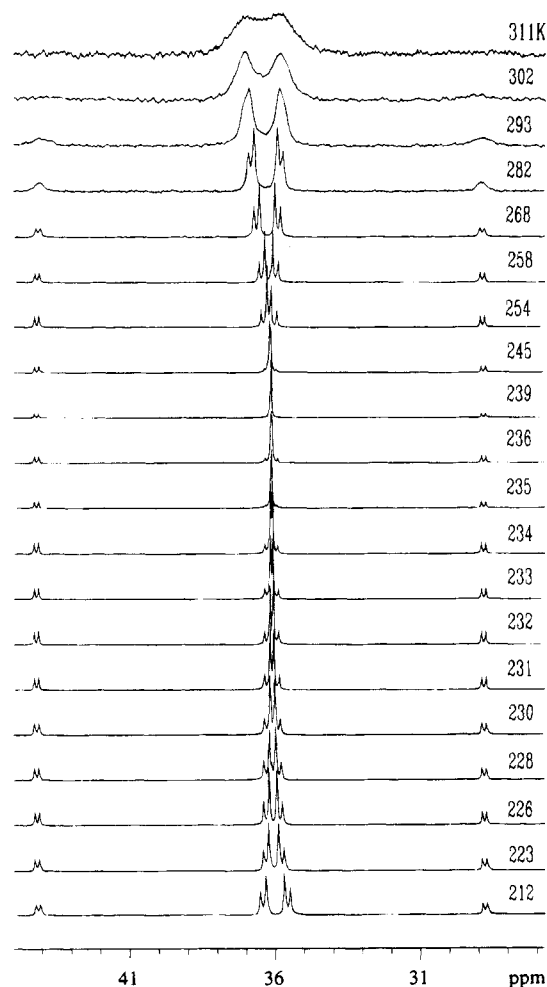


Figure 3. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compound **3a** in CD_2Cl_2 (161.98 MHz).

and II in a 3:1 ratio are observed in the considered temperature range. This effect is strongly dependent on the solvent, e.g. in CDCl_3 isomer II is not observed. Isomer I displays an AB pattern. The small coupling constant ($^2J_{\text{PP}} = 32.6$ Hz) corroborates with *cis*-arrangement of the phosphines confirming the structure obtained by X-ray analysis. A further proof for this coordination geometry can be drawn from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3a,b** displaying a characteristic coupling pattern

for the vinylic α -carbon caused from two phosphines which are *cis*-coordinated to the vinylidene unit. Inspection of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra reported in Figure 3 reveals that the temperature affects the NMR parameters of isomer I. In particular, we note a marked dependence of the chemical shifts of both phosphines with the temperature, whereas the coupling constant remains unchanged. Due to this phenomenon, the two resonances coincide at ca. 239 K and above this temperature they exchange their position. A similar effect was already reported.²⁵ Moreover the signals of isomer I start to broaden at ca. 282 K (Figure 3). Coalescence is nearly reached at 311 K but further increasing of the temperature is restricted due to the boiling point of CD_2Cl_2 . We therefore estimate the coalescence at ca. 315 K from which a ΔG_{315}^\ddagger value of 60.1 kJ mol $^{-1}$ is calculated.¹⁹ Due to the ether–oxygen donor which is *trans*-positioned to a phosphine, isomer I prevents a simple “opening and closing” mechanism of the ether–phosphines resulting in a relatively high coalescence temperature and ΔG^\ddagger value. It also cannot be ruled out that a hindered rotation of the vinylidene unit could be responsible for this coalescence phenomenon.²⁶ On the basis of our spectroscopic data it is not possible to distinguish between both exchange mechanisms.

In order to get an insight into the thermodynamic parameters of the process we performed a line shape analysis using a modified version of DNMR5²⁷ and the program ACTPAR²⁸ (Figure 4). It was necessary to iterate the chemical shifts of the resonances for each temperature due to their linear temperature dependence. We found that the simulated resonances confirm the extrapolated values of the chemical shifts. The comparison of the obtained thermodynamic parameters ($\Delta H^\ddagger = 40.2 \pm 7.9$ kJ mol $^{-1}$ and $\Delta S^\ddagger = -65.8 \pm 27.3$ J (mol K) $^{-1}$) with reported results indicate a relatively weak ruthenium–oxygen bond.⁴ The large error in the estimation of ΔS^\ddagger prevents us from proposing a mechanism for the exchange phenomenon. Isomer I of **3a,b** is found to be the thermodynamically most stable configuration as established for the analogous *cis*- $\text{Cl}_2\text{-Ru(CO)(P}^\sim\text{O)(P}^\sim\text{O)}$ complex.¹¹

Isomer II reveals an AX pattern. Two sets of signals account for a chelated (downfield resonance) and an open-chain (high-field region) ether–phosphine with a small coupling constant ($^2J_{\text{PP}} = 24.4$ Hz), indicating *cis*-arrangement of the phosphine ligands. We propose both ether–phosphines *trans*-positioned to chlorine and the vinylidene unit *trans*-arranged to oxygen. The broadening of the signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra above 268 K can be explained by a coalescence at ca. 303 K (Figure 3) from which a ΔG_{303}^\ddagger value of 52.5 kJ mol $^{-1}$ is calculated.¹⁹ This dynamic behavior could be traced back to an exchange process of the ether–phosphines arranged to compete for the vacant coordination site (Scheme 3). The simple “opening and closing” mechanism explains the lower ΔG^\ddagger value of isomer II compared to isomer I.

In contrast to the vinylidene complexes **3a,b** (*vide supra*), compound **3c** is prepared starting from a solution of **1c** and phenylacetylene in toluene, which is irradiated at ambient temperature with a mercury lamp. The orange complex **3c** is obtained in almost quantitative yield as an air-stable solid which

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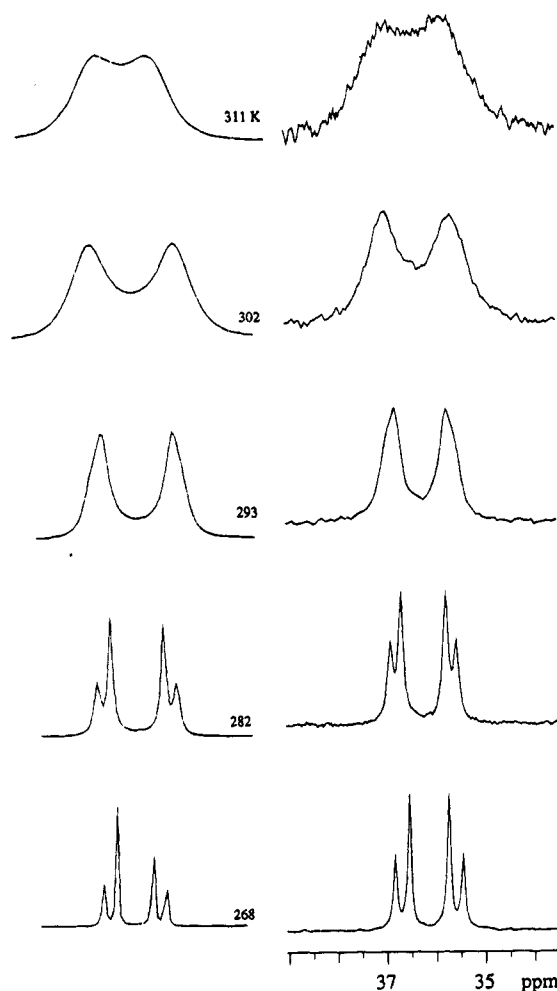


Figure 4. Computed spectra for the AB spin system of isomer (II) of **3a** (left) and the corresponding variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CD_2Cl_2 (161.98 MHz).

is readily soluble in most common organic solvents but is insoluble in saturated hydrocarbons. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3c** at -80°C displays an AB pattern at 28.0 and 2.8 ppm (each d, $^2J_{\text{PP}} = 358\text{ Hz}$), attributed to a chelated ether-phosphine (downfield doublet) and an open-chain ligand (doublet at higher field). The large coupling constant is consistent with a *trans*-arrangement of the bulky phosphines.²⁹ Complex **3c** reveals fluxional behavior in solution at remarkably low temperature. By increasing the temperature, both doublets first broaden and then coalesce at ca. 231 K from which a ΔG_{231}^\ddagger value of 41.8 kJ mol^{-1} is calculated.¹⁹ At room temperature a sharp singlet at 15.9 ppm is observed. This dynamic process may be rationalized by the "opening and closing" mechanism³ of the ether-phosphines competing for the vacant coordination site. The IR spectrum of **3c** exhibits a strong band at 1591 cm^{-1} assigned to the $\text{C}=\text{C}$ stretching mode. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3c** displays the highly deshielded vinylic C_α triplet ($\delta_{\text{C}} = 350.2\text{ ppm}$, $^2J_{\text{PC}} = 16.0\text{ Hz}$) and a singlet ($\delta_{\text{C}} = 109.2\text{ ppm}$) for the vinylic C_β . The ^1H NMR spectrum of **3c** shows a triplet ($\delta_{\text{H}} = 4.34\text{ ppm}$, $^4J_{\text{PH}} = 3.7\text{ Hz}$) for the vinylic proton, providing further evidence for the η^1 -vinylidene unit. These NMR data are consistent with related η^1 -vinylidene-ruthenium(II) complexes.^{23a,b}

The proposed *trans*-configuration is proved by an X-ray structural analysis of **3c** (Figure 5). Selected bond distances and angles are presented in Table 2. The Ru–C(1) distance

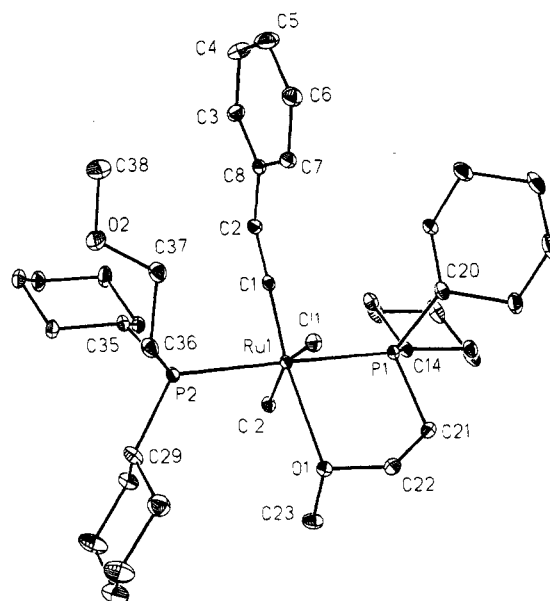


Figure 5. ORTEP plot of the molecular structure of compound **3c**. The cyclohexyl groups are not labeled.

($178.0(3)\text{ pm}$) is similar to that of compound **3a**. The conspicuous long ruthenium–oxygen bond ($241.1(2)\text{ pm}$) is caused by a strong *trans*-influence of the vinylidene moiety, leading to a weak Ru–O contact. This fact is also established in the low coalescence temperature of the variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3c** (*vide supra*). The bond angles $\text{O}(1)\text{--Ru--C}(1)$, $\text{P}(1)\text{--Ru--P}(2)$, and $\text{Ru--C}(1)\text{--C}(2)$, respectively, are almost linear.

Reactions of 1a–c with Acetonitrile. Treatment of dichloromethane solutions of **1a–c** with acetonitrile at ambient temperature results in the formation of the corresponding acetonitrile complexes **4a–c** which is accompanied by a color change from red to yellow (Scheme 1). With the exception of the yellow-green complex **4c** compounds **4a, b** are moderately air-stable, orange products. **4a–c** are readily soluble in chlorinated organic solvents in which the CH_3CN ligand slowly dissociates. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra reveal an AB pattern for each compound **4a–c** displaying low coupling constants which are in favor of *cis*-phosphines being $\eta^2(\text{O,P})$ and $\eta^1(\text{P})$ coordinated, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **4a–c** two sets of signals are observed belonging to different oxygen adjacent carbon atoms which are incorporated in both different coordinated ether-phosphines. Compared to uncoordinated CH_3CN , the corresponding resonances for the methyl and the nitrile carbon atoms are slightly shifted downfield.³⁰ The proposed structure (Scheme 1) is analogous to those of **2a, 3a**, and **10b**. Owing to the coordination capability of the CH_3CN ligand, we observed a competition between this ligand and the intramolecular chelation of the ether-phosphine.

Reaction of 1c with Carbon Disulfide. Whereas **1a, b** are inert toward CS_2 , a solution of **1c** in toluene reacts readily at elevated temperature to yield the corresponding CS_2 complex **5c**. The reaction is accompanied by a color change from red to almost black (Scheme 1). Compound **5c** is an air-stable, dark purple solid, and is readily soluble in polar organic solvents such as toluene, CH_2Cl_2 , and ethanol but is insoluble in saturated hydrocarbons. A downfield singlet ($\delta_{\text{P}} = 51.2\text{ ppm}$) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is assigned to a chelated ether-phosphine whereas the signal at higher field ($\delta_{\text{P}} = 24.5\text{ ppm}$) is in the range of open-chain ether-phosphines. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5c** displays two sets of resonances for the ether

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oxygen adjacent carbon atoms confirming two nonequivalent phosphine ligands and moreover a doublet ($\delta_{\text{C}} = 211.7$ ppm, $^1J_{\text{PC}} = 34.5$ Hz) in the downfield region. A medium intensive absorption in the IR spectrum of **5c** at 1006 cm^{-1} is characteristic for a $\text{M}-\text{S}_2\text{CX}$ unit.³¹ To sum up these spectroscopic data it can be said that carbon disulfide inserts into a $\text{Ru}-\text{P}$ bond to form the zwitterionic $-\text{S}_2\text{CP}\sim\text{O}^+$ unit acting as a chelating ligand (Scheme 1). This insertion reaction is only observed with basic phosphines.³²

Reaction of 1c with Carbon Monoxide. According to the synthesis of the well-known all-*trans*-complexes $\text{Cl}_2\text{Ru}(\text{CO})_2(\text{P}(\text{O})_2)_2$,¹¹ the ruthenium oxygen bond of **1c** is easily cleaved by stirring a solution of **1c** in dichloromethane under an atmosphere of CO at ambient temperature. The yellow, air-stable dicarbonyl complex **6c** is easily soluble in common organic solvents and shows marked loss of carbon monoxide. Owing to two equivalent η^1 -coordinated phosphines a single resonance at 19.3 ppm is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6c**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays a triplet ($\delta_{\text{C}} = 199.7$ ppm, $^2J_{\text{PC}} = 12.6$ Hz) for the CO carbon atom and two single resonances at 68.1 and 58.3 ppm for the oxygen adjacent carbon atoms which are in the range of open-chain ether-phosphines. A strong absorption at 1981 cm^{-1} in the IR spectrum of **6c** confirms *trans*-coordination of carbon monoxide. Due to the steric demand of the cyclohexyl groups as it is established for related complexes a *trans*-arrangement of the phosphines is preferred.^{11,18}

The light yellow, air-stable monocarbonyl complex **7c** is obtained by bubbling a stream of argon through a solution of **6c** in dichloromethane at elevated temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7c** reveals an AB pattern at 47.0 and 11.7 ppm and the large coupling constant ($^2J_{\text{PP}} = 303$ Hz) indicates a *trans*-configuration of the ether-phosphines. This coordination geometry is also supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7c** (see Experimental Section). The strong CO absorption at 1938 cm^{-1} in the IR spectrum is markedly shifted to lower wave numbers as it is expected for the more basic ruthenium central atom and confirms the CO ligand being *trans*-arranged to oxygen. The variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **7c** point to a fluxional behavior in solution. Whereas an AB pattern is observed at -30°C , the resonances broaden by increasing the temperature until the signals coalesce at 28°C , from which a ΔG^\ddagger value of 54.4 kJ mol^{-1} is calculated.¹⁹

Reactions of 1a–c with *tert*-Butyl Isocyanide. If CH_2Cl_2 or toluene solutions of **1a–c** are allowed to react with excess *tert*-butyl isocyanide the bis(isocyanide)ruthenium(II) complexes **8a–c** are accessible. The reactions were monitored by a color change from red to yellow (**8a,b**) and green (**8c**), respectively (Scheme 2). **8a–c** represent air-stable compounds which are readily soluble in chlorinated solvents and acetone but are rather insoluble in nonpolar solvents. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **8a–c** display singlets for each complex which are in the range of open-chain ether-phosphines.¹⁸ The $\eta^1(\text{P})$ coordination of the phosphine ligands is also supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **8a–c**, which reveal typical resonances for the noncoordinated ether moiety. Low intensity multiplets in the low field region are ascribed to the corresponding isocyanide carbon atoms. The appearance of one strong absorption in the IR spectra of **8a–c** at 2124, 2125, and 2101 cm^{-1} , respectively, is typical for a *trans*-arrangement of the isocyanide ligands. Moreover, two absorptions in the far-IR spectra of **8a–c** are consistent with *cis*-chlorines at the ruthenium center. Due to

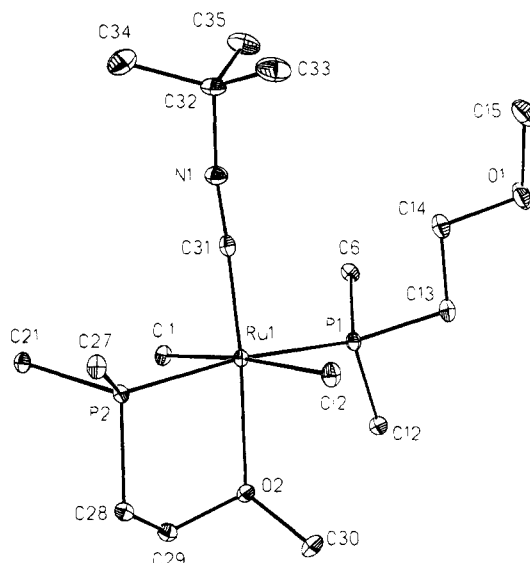


Figure 6. ORTEP plot of compound **9a**. The phenyl groups are omitted for clarity.

the bulky *tert*-butyl groups and in contrast to the corresponding *cis,cis,trans*-dicarbonylruthenium (II) complexes⁴ wherein the sterically demanding phosphines are *trans*-positioned, we propose a *cis,cis,trans*-configuration for **8a–c** with *tert*-butyl isocyanide in a *trans*-position.

Whereas the monoisocyanide complex **9a** is available by stirring a 1:1 mixture of *tert*-butyl isocyanide and **1a** in dichloromethane the congener **9c** is better obtained by a ligand symproportionation of stoichiometric amounts of **1c** and **8c** in refluxing toluene (Scheme 2). Both complexes are yellow, air-stable, and are soluble in polar organic solvents but rather insoluble in nonpolar solvents. Owing to a chelated and an open-chain ether-phosphine, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for each complex **9a, c** display an AB pattern. The large coupling constants (**9a**: $^2J_{\text{PP}} = 350$ Hz; **9c**: $^2J_{\text{PP}} = 315$ Hz) indicate a *trans*-arrangement of the ether-phosphines. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **9a, c** provide further evidence for that bonding mode. Multiplets for the corresponding isocyanide carbon atoms show coupling patterns which are characteristic for *cis*-positioned phosphines. Remarkably, the IR spectra of **9a, c** (KBr) reveal two ($\text{C}\equiv\text{N}$) bands at 2099 and 2068 cm^{-1} for **9a** and at 2091 and 2059 cm^{-1} for **9c**. Both absorptions appear also in the corresponding IR spectra of **9a, c** in solution (CH_2Cl_2). In order to solve this phenomenon we performed variable-temperature IR spectroscopic investigations in the solid state with the sample of **9a**. The intensities of these absorptions are not markedly changed in the considered temperature range from 78 up to 296 K, however, to such an extent that Fermi resonance may be excluded. To ensure the configuration at the central atom and to distinguish between possible conformers the structure of **9a** has been determined twice by an X-ray structural analysis. Both investigations result in the same structure and the single crystals show identical IR spectra. The ORTEP drawing is shown in Figure 6. Table 2 contains selected bond distances and angles. The ruthenium center is octahedrally coordinated with *trans*-phosphines and *trans*-chlorines, and the isocyanide ligand is *trans*-arranged to the chelated ether oxygen atom. The $\text{Ru}(1)-\text{C}(31)$ ($186.8(2)\text{ pm}$) and $\text{Ru}(1)-\text{O}(2)$ bond lengths ($224.8(14)\text{ pm}$) are slightly shorter than the reported values in similar complexes.³³ The five-membered chelate ring has an

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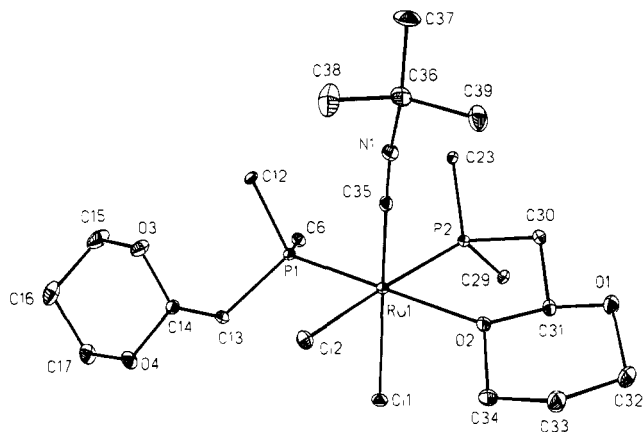


Figure 7. ORTEP presentation of compound **10b**. The phenyl groups are omitted for clarity.

envelope conformation wherein the angle between the planes which are formed by the atoms C(28)–C(29)–O(2) and C(28)–P(2)–Ru(1)–O(2) is 132.4° . The N(1)–C(31)–Ru(1) bond angle ($177.0(2)^\circ$) is almost linear.

In order to study the fluxional behavior of **9a,c**, temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic investigations have been carried out. Each complex displays an AB pattern at -30°C . The signals first broaden by raising the temperature and finally coalesce at 313 K (**9a**) and at 283 K (**9c**), respectively. The ΔG_c^\ddagger values were calculated with the approximate equation: $\Delta G_c^\ddagger = RT_c(22.96 + \ln T_c/\delta\nu)^{19}$ for **9a**, 56.9 kJ mol^{-1} , and for **9c**, 51.1 kJ mol^{-1} . The lower coalescence temperature of **9c** accounts for a weaker ruthenium ether oxygen bond which may be rationalized by the more basic ruthenium center in **9c**.

The action of equimolar amounts of the starting material **1a,b** on the bis(isocyanide) complexes **8a,b** in refluxing toluene affords the yellow, air-stable species **10a,b** which are readily soluble in chlorinated solvents and rather insoluble in nonpolar solvents. The AB patterns in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a,b** show small coupling constants which are in agreement with a *cis*-arrangement of $\eta^2(\text{O,P})$ and $\eta^1(\text{P})$ coordinated ether-phosphines. This coordination mode is confirmed by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **10a, b** in which characteristic resonances for nonequivalent ether moieties are observed. The downfield multiplets are attributed to the isocyanide carbon atoms displaying typical coupling patterns for *cis*-positioned phosphines. In contrast to the *trans*-phosphine complexes **9a, c**, only one band is observed in the isocyanide region of the IR spectra of **10a, b**.

For a detailed structural characterization an X-ray structural analysis has been performed with the example of **10b**. Figure 7 shows an ORTEP plot of **10b**. Selected bond distances and angles are summarized in Table 2. The structural determination confirms the spectroscopic data with *cis*-phosphines and *cis*-chlorines at the ruthenium center. The isocyanide ligand is *trans*-arranged to a chlorine. The Ru(1)–C(35) bond length ($191.8(3)\text{ pm}$) is in the expected range.³³ Due to the bulky phenyl groups at P(1) the bond angle C(35)–Ru(1)–Cl(1) ($170.6(9)^\circ$) is slightly bent.

The mixed carbon monoxide and isocyanide complexes **11a,c** are readily available by the reaction of **9a,c** with carbon monoxide, **11a** is also accessible by treatment of a solution of **10a** with CO (Scheme 2). It should be mentioned that the ruthenium–ether–oxygen contact of **9a** and **10a** is more easily cleaved than the corresponding bond in **9c**. Moreover, the Ru–O bond rupture of **10b** is achieved by bubbling carbon monoxide through a solution of **10b** to yield **12b** (Scheme 2).

11a,c are light yellow, air-stable compounds whereas **12b** is almost colorless. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **11a,c** and **12b** display singlets in the characteristic range of $\eta^1(\text{P})$ coordinated ether–phosphine ruthenium(II) complexes.^{4,11} Highly deshielded triplets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **11a,c** and **12b** are assigned to the CO carbon atoms. The characteristic coupling pattern is due to two equivalent *cis*-arranged phosphine ligands. The isocyanide carbon atoms give rise to multiplets in the expected range of the corresponding spectra. Moreover, the spectra of **11a,c** and **12b** show one set of resonances for the oxygen adjacent carbon atoms of the ether moiety which is traced back to open-chain ether–phosphines. Two strong absorptions arise in the $1800\text{--}2200\text{ cm}^{-1}$ region of the IR spectra of **11a,c** and **12b**, whereas the absorption at higher wave numbers is attributed to the isocyanide moiety and the band at lower frequency is assigned to carbon monoxide. The arrangement of the chlorines is unambiguously proved by the far-IR spectra of **11a** and **12b**, displaying only one RuCl_2 band at 320 cm^{-1} for **11a** and two absorptions at 312 and 280 cm^{-1} for **12b**, respectively. We therefore propose *trans*-chlorines and *trans*-phosphines for the complexes **11a,c** and *cis*-chlorines and *cis*-phosphines for **12b**.

Conclusion

The present study describes the chemical behavior of the bis-(chelate)ruthenium(II) complexes **1a–c** with different basic ether–phosphine ligands toward a variety of small molecules. To estimate the influence of the Lewis basicity at the ruthenium center and the Ru–O bond strength toward incoming substrates, the ligands $\text{Ph}_2\text{PCH}_2\text{C}_4\text{H}_7\text{O}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$, and $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ have been employed. The $\eta^2(\text{O,P})$ ether–phosphine complexes **1a–c** make available valuable pseudo-14-electron precursors only weakly protected by intramolecular chelation of the ether moieties. Hence, the facile cleavage of one or both Ru–O bonds of the chelates is applicable to activate small molecules such as sulfur dioxide, phenylacetylene, acetonitrile, carbon disulfide, carbon monoxide, and *tert*-butyl isocyanide. Carbon disulfide reacts only with the most Lewis basic starting complex **1c** and is inserted into one Ru–P bond with the formation of the phosphoniodithiocarboxylate compound **5c**. Most reactions afford only moderate conditions and lead to almost quantitative yields. To sum up the results it can be said that the ease of the Ru–O bond rupture of the bis(chelates) and the stability of the received substrate complexes, respectively, is in the order $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3 > \text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3 > \text{Ph}_2\text{PCH}_2\text{C}_4\text{H}_7\text{O}_2$. All exchange phenomena are coupled with the “opening and closing” mechanism of the employed ether–phosphines.

Acknowledgment. M.G. acknowledges the Land Baden-Württemberg for the award of a Ph.D. Fellowship (Landesgraduiertenförderungsgesetz). The support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged. We appreciate the help of Prof. Dr. V. Hoffmann, Institut für Physikalische und Theoretische Chemie, Universität Tübingen, for the implementation of the temperature-dependent IR spectra. We thank the BASF Aktiengesellschaft for valuable starting materials.

Supporting Information Available: Tables of crystallographic data, complete atomic parameters, anisotropic thermal parameters, interatomic distances and angles, hydrogen atom coordinates, and isotropic thermal parameters for **2a, 3a, 3c, 9a**, and **10b** and a table of least-squares planes for **9a** (35 pages). Ordering information is given on any current masthead page.