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Reversible and Irreversible Coordination of Small Molecules to the Cp*Ru Fragment by a Facile Cleavage of the Ruthenium−Oxygen Bond of η^2 $P^\frown O$-Chelated (1,3-Dioxan-2-ylmethyl)diphenylphosphine

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The complex [Cp*Ru($P\sim O$)($P^\frown O$)][BPh_4] (**1**; Cp* = η^5-C_5Me_5; $P^\frown O$ = η^2(O,P)-chelated (1,3-dioxan-2-ylmethyl)diphenylphosphine; $P\sim O$ = η^1(P)-coordinated) is shown to undergo a facile cleavage of its intramolecular ether moiety by reaction with a variety of small molecules. Compound **1** readily takes up ethene whereupon the η^2-ethene complex [Cp*Ru($P\sim O$)$_2$(η^2-$H_2C{=}CH_2$)][BPh_4] (**2**) is generated which is only stable under an atmosphere of C_2H_4. If **2** is stirred under an atmosphere of argon, it is reversibly converted into the starting compound **1**. Hydrogenation of 1-hexene to *n*-hexane with complex **1** proceeds catalytically. Conversion rates are acceptable at elevated temperatures (>80 °C). The reaction of **1** with sulfur dioxide, carbon disulfide, oxygen, phenylacetylene, and diphenyldiazomethane results in the irreversible coordination of the corresponding molecule to the metal affording the stable complexes [Cp*Ru($P\sim O$)$_2$(η^1-SO_2)][BPh_4] (**3**), [Cp*Ru($P\sim O$)$_2$(CS)][BPh_4] (**4**), [Cp*Ru($P\sim O$)$_2$(η^2-CS_2)][BPh_4] (**5**), [Cp*Ru($P\sim O$)$_2$(O_2)][BPh_4] (**6**), [Cp*Ru($P\sim O$)$_2$(C=CHPh)][BPh_4] (**7**), and [Cp*Ru($P\sim O$)$_2$(N_2CPh_2)][BPh_4] (**8**), respectively. All compounds are obtained in excellent yields under mild reaction conditions. The structures of **3**, **4**, and **6** were determined by single-crystal X-ray diffraction. Aside from the coordinated small molecules, the structures are nearly identical and the compounds crystallize in the same monoclinic space group $P2_1/c$ with Z = 4. The cell dimensions are as follows: for **3**, a = 9.526(6) Å, b = 17.195(9) Å, c = 38.23(2) Å, β = 94.73(5)°; for **4**, a = 9.847(4) Å, b = 17.368(5) Å, c = 38.394(14) Å, β = 94.57(1)°; for **6**, a = 19.47(4) Å, b = 13.23(2) Å, c = 22.88(4) Å, β = 113.36(1)°.

Introduction

The chemistry of the cyclopentadienylbis(phosphine)ruthenium auxiliary has been an area of active research interest in the last years. The reactivity of this system toward a variety of anionic and neutral ligands has led to a wide range of interesting derivatives.[1] Attention has been drawn to the fact that replacement of Cp by Cp* reduces the Lewis acidity of the system due to both electronic and steric effects.[2,3] The electron-rich ruthenium center has been anticipated to play a significant role in the discovery of new reactivity patterns.

In a recent study we reported about cyclopentadienyl- and (pentamethylcyclopentadienyl)ruthenium(II) complexes containing monodentate ($P\sim O$) and bidentate ($P^\frown O$) ether−phosphines ($P\sim O$ = η^1 (P)-coordinated ligand; $P^\frown O$ = η^2 (O,P)-chelated ligand).[4] These ligands form a close metal−phosphorus contact and a weaker metal−oxygen bond. The ruthenium−oxygen bond strength in complexes of the type [(η^5-C_5R_5)Ru($P\sim O$)($P^\frown O$)]$^+$ (R = H; CH_3) was found to be strongly dependent on the use of the Cp or the Cp* ligand. This was proved by variable-temperature ^{31}P NMR spectroscopic investigations showing fluxional behavior only for the Cp* complexes. From line shape analyses of ^{31}P DNMR spectroscopic studies we determined the thermodynamic parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta G_c^\ddagger$, and $\Delta G_{298}^\ddagger$ in dependence on the kind of the ether moieties, the ring size of the cyclic ethers, and the number and the position of the ether atoms in the ring. One of the lowest $\Delta H^\ddagger$ values, which indicate the Ru−O bond strength, was found for the complex with the (1,3-dioxan-2-ylmethyl)diphenylphosphine ligand.[4] Therefore, in this paper our investigations are focused on the coordination of small molecules to [Cp*Ru($P\sim O$)($P^\frown O$)][BPh_4] (**1**) (O,P = (1,3-dioxan-2-ylmethyl)diphenylphosphine). We are able to present a reactive precursor having a vacant coordination site at the ruthenium center due to the very weak Ru−O interaction. A facile cleavage of the intramolecular ether moiety takes place if **1** is reacted with ethene, phenylacetylene, oxygen, sulfur dioxide, and carbon disulfide. All reactions are carried out under mild conditions and in quantitative yields in most of the cases.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR data were obtained with a Bruker IFS

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48 instrument. FD mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV, 60 °C), modified by AMD; FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (10 kV, 50 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; S analyses were carried out according to Schöniger[5] and analyzed as described by Wagner.[6] Ru was determined according to the literature.[7] ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 32.44 MHz, external standard (coaxial insert) 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. The temperatures of the ^{31}P DNMR experiment of **2** were measured as recently published[4] and are considered accurate ±1 K. ^{1}H and ^{13}C{^{1}H} NMR were measured with Bruker AC 80, Bruker AC 250, and Bruker AMX 400 spectrometers at 80.13 and 20.15, 250.13 and 62.90, and 400.13 and 100.62 MHz, respectively. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to TMS. The starting complex **1** was synthesized as previously described.[4]

Hydrogenations. Air was removed from a 100 mL stainless steel autoclave containing the catalyst and the substrate. Hydrogen was added up to the desired pressure, and the autoclave was then heated to the selected temperature. The stirring rate was kept constant in all experiments. The conversion was determined by GC analysis of the reaction mixture (DB WAX column).

Bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](η^2-ethene)(pentamethylcyclopentadienyl)ruthenium(II) Tetraphenylborate (2). A solution of **1** (500 mg, 0.44 mmol) in 20 mL of dichloromethane was stirred at ambient temperature under an atmosphere of ethene. The dark red solution turned to bright yellow after 10 min. **2** is only stable in solution under an atmosphere of C_2H_4 and cannot be isolated. ^{31}P{^{1}H} NMR (32.44 MHz, CH_2Cl_2, −50 °C): δ 38.6, 33.4 (d, $^{2}J_{PP}$ = 38.0 Hz). ^{13}C{^{1}H} NMR (20.15 MHz, CD_2Cl_2, 22 °C): δ 164.5 (q, $^{1}J_{CB}$ = 48.6 Hz, *ipso*-C of BPh_4), 136.4−122.1 (m, C−Ph), 99.6 (s, CH), 98.3 (s, C_5Me$_5$), 67.0 (s, OCH_2CH$_2$), 46.9 (s, C=C), 32.9 (m, J = 22.2 Hz,[8] PCH_2), 25.3 (s, OCH$_2$$CH_2$), 10.6 (s, C$_5$$Me_5$).

Bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](pentamethylcyclopentadienyl)(η^1-*S*-sulfur dioxide)ruthenium(II) Tetraphenylborate (3). Sulfur dioxide was bubbled into a solution of **1** (350 mg, 0.31 mmol) in 20 mL of dichloromethane at ambient temperature. A spontaneous color change from dark red to orange occurred. After 5 min of stirring the solvent was removed under vacuum. The residue was washed with 10 mL of *n*-hexane to give a yellow precipitate, which was collected by filtration (G3) and dried in vacuo to yield 369 mg (100%) of **3**; mp 122 °C dec; MS (FD, 60 °C) *m/e* 873 [M$^+$ − BPh_4]. Anal. Calcd (found) for $C_{68}H_{73}BO_6P_2RuS$: C, 68.50 (68.84); H, 6.17 (6.52); Ru, 8.48 (8.35); S, 2.69 (2.78). IR (KBr, cm^{-1}): $\nu(SO_2)$ 1277 (m), 1109 (vs). ^{31}P{^{1}H} NMR (32.44 MHz, CH_2Cl_2, −30 °C): δ 23.5 (s). ^{13}C{^{1}H} NMR (20.15 MHz, CD_2Cl_2, 22 °C): δ 164.2 (q, $^{1}J_{CB}$ = 48.6 Hz, *ipso*-C of BPh_4), 136.2−121.4 (m, C−Ph), 104.3 (s, C_5Me$_5$), 98.9 (s, CH), 66.5 (s, OCH_2CH$_2$), 35.1 (m, J = 28.4 Hz,[8] PCH_2), 24.8 (s, OCH$_2$$CH_2$), 9.8 (s, C$_5$$Me_5$).

Bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](pentamethylcyclopentadienyl)(thiocarbonyl)ruthenium(II) Tetraphenylborate (4). A solution of **1** (526 mg, 0.47 mmol) in 20 mL of dichloromethane was reacted with a mixture of 126 mg (1.65 mmol) of carbon disulfide and 436 mg (1.65 mmol) of triphenylphosphine in 5 mL of CH_2Cl_2 at ambient temperature. Almost immediately the reaction mixture became dark purple. After the solution was stirred overnight, the purple color faded to orange-brown. The reaction mixture was purified by chromatography on activated silica gel (length of column 25 cm). With diethyl ether as eluent excess PPh_3 and $SPPh_3$ were eluated. The orange-brown fraction which contained **4** together with mixed phosphine η^2-CS_2 complexes was eluated with 1/1 CH_2Cl_2/diethyl ether and evaporated to dryness. The remaining brownish solid was redissolved in 10 mL of dichloromethane. Addition of diethyl ether resulted in the precipitation of bright yellow crystals of **4**: Yield 306 mg (56%); mp 206−207 °C dec; MS (FD, 60 °C) *m/e* 853 [M$^+$ − BPh_4]. Anal. Calcd (found) for $C_{69}H_{73}BO_4P_2RuS$: C, 70.70 (70.41); H, 6.28 (6.22); Ru, 8.62 (8.48); S, 2.74 (2.42). IR (KBr, cm^{-1}): ν(CS) 1264 (vs). ^{31}P{^{1}H} NMR (32.44 MHz, CH_2Cl_2, −30 °C): δ 29.2 (s). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 22 °C): δ 314.0 (t, $^{2}J_{PC}$ = 16.1 Hz, CS), 164.1 (q, $^{1}J_{CB}$ = 49.3 Hz, *ipso*-C of BPh_4), 136.1−121.3 (m, C−Ph), 102.1 (s, C_5Me$_5$), 99.1 (s, CH), 66.6 (s, OCH_2CH$_2$), 34.7 (m, J = 29.6 Hz,[8] PCH_2), 24.6 (s, OCH$_2$$CH_2$), 9.0 (s, C$_5$$Me_5$).

(η^2-Carbon disulfide)bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](pentamethylcyclopentadienyl)ruthenium(II) Tetraphenylborate (5). A solution of **1** (580 mg, 0.51 mmol) in 20 mL of dichloromethane was treated with a mixture of carbon disulfide (126 mg, 1.65 mmol) and the O,P ligand (473 mg, 1.65 mmol) in 5 mL of dichloromethane at ambient temperature. Instantaneously the reaction mixture turned to dark purple. After the solution was stirred overnight, the purple color faded to orange-brown. The reaction mixture was purified by chromatography on activated silica gel (length of column 25 cm). Excess O,P ligand and ether−phosphine sulfide were eluated with diethyl ether as eluent. The orange-brown fraction which contained **5** together with **4** was eluated with 1/1 CH_2Cl_2/diethyl ether and was evaporated to dryness. The brownish solid was redissolved in 10 mL of dichloromethane, and **4** was separated by precipitation with diethyl ether. The remaining orange-brown solution was evaporated under vacuum and washed with 10 mL of *n*-hexane to give an orange-brown precipitate. The precipitate was collected by filtration (G3) and dried in vacuo: Yield 370 mg (61%); mp >77 °C dec; MS (FAB, 50 °C) *m/e* 885 [M$^+$ − BPh_4]. Anal. Calcd (found) for $C_{69}H_{73}BO_4P_2RuS_2$: C, 68.82 (68.61); H, 6.11 (5.84); Ru, 8.39 (8.16); S, 5.32 (5.39). IR (KBr, cm^{-1}): ν(CS) 1266 (s). ^{31}P{^{1}H} NMR (32.44 MHz, CH_2Cl_2, −30 °C): δ 39.7, 4.8 (d, $^{2}J_{PP}$ = 12.2 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 22 °C): δ 201.1 (dd, $^{2}J_{PC}$ = 40.2 and 9.7 Hz, CS_2), 164.3 (q, $^{1}J_{CB}$ = 49.3 Hz, *ipso*-C of BPh_4), 136.3−121.4 (m, C−Ph), 100.6, 96.0 (s, CH), 90.4 (s, C_5Me$_5$), 66.8 (s, OCH_2CH$_2$), 35.1, 29.1 (d, $^{1}J_{PC}$ = 23.6 and 55.5 Hz, PCH_2), 25.0, 24.4 (s, OCH$_2$$CH_2$), 10.5 (s, C$_5$$Me_5$).

Bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](dioxygen)(pentamethylcyclopentadienyl)ruthenium(II) Tetraphenylborate (6). A solution of **1** (500 mg, 0.44 mmol) in 20 mL of dichloromethane was treated with oxygen (1 bar) at room temperature until a dark yellow solution was obtained. The reaction takes approximately 15 min. The solvent was removed completely under vacuum. The residue was washed with 10 mL of *n*-hexane to give a dark yellow precipitate which was collected by filtration (G3) and dried in vacuo to yield 510 mg (100%); mp 132 °C dec; MS (FD, 60 °C) *m/e* 841 [M$^+$ − BPh_4]. Anal. Calcd (found) for $C_{68}H_{73}BO_6P_2Ru$: C, 70.40 (70.02); H, 6.34 (6.40); Ru, 8.71 (8.80). ^{31}P{^{1}H} NMR (32.44 MHz, CH_2Cl_2, −30 °C): δ 18.5 (s). ^{13}C{^{1}H} NMR (20.15 MHz, $CDCl_3$, 22 °C): δ 164.2 (q, $^{1}J_{CB}$ = 49.6 Hz, *ipso*-C of BPh_4), 136.2−121.3 (m, C-Ph), 107.4 (s, C_5Me$_5$), 99.2 (s, CH), 66.7 (s, OCH_2CH$_2$), 28.7 (m, J = 31.0 Hz,[8] PCH_2), 24.6 (s, OCH$_2$$CH_2$), 9.4 (s, C$_5$$Me_5$).

(Benzylidenecarbene)bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](pentamethylcyclopentadienyl)ruthenium(II) Tetraphenylborate (7). Addition of phenylacetylene (93 mg, 0.91 mmol) to a solution of **1** (380 mg, 0.34 mmol) in 20 mL of dichloromethane, followed by a short period of stirring at room temperature, gave a deep red solution, which was evaporated to dryness. The residue was washed with 10 mL of *n*-pentane to give a pale red precipitate. The precipitate was collected by filtration (G3), washed with *n*-pentane, and dried in vacuo yielding 418 mg (100%); mp 108−109 °C dec; MS (FD, 60 °C) *m/e* 912 [M$^+$ − BPh_4]. Anal.

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[8] A part of an AXX′ spectrum, $J = |^{1}J_{PC} + {}^{3}J_{PC}|$.

Table 1. Crystal Data and Refinement Details for Compounds 3, 4, and 6

	compound		
	3·2CH$_2$Cl$_2$	**4**·2CH$_2$Cl$_2$	**6**
formula	$C_{68}H_{73}BO_6P_2RuS$	$C_{69}H_{73}BO_4P_2RuS$	$C_{68}H_{73}BO_6P_2Ru$
fw	1362.0	1342.0	1160.1
color	red plates	yellow cubes	orange plates
cryst dimens	0.2 × 0.2 × 0.3	0.25 × 0.25 × 0.5	0.2 × 0.25 × 0.25
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	9.526(6)	9.847(4)	19.47(4)
b, Å	17.195(9)	17.368(5)	13.23(2)
c, Å	38.23(2)	38.394(14)	22.88(4)
β, deg	94.73(5)	94.57(1)	113.36(1)
V, Å^3	6241(6)	6546(4)	5408(16)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.450	1.362	1.425
T, °C	−100	−100	−100
$F(000)$, e	2832	2792	2432
μ(Mo Kα), mm^{-1}	0.561	0.532	0.406
2θ limits, deg	4−50	4−50	4−50
no. of reflns measd	21 968	23 041	18 970
no. of unique data with $I \geq 2\sigma(I)$	6417	5950	2221
no. of variables	767	758	704
S	1.33	1.02	0.77
R_1[a]	0.047	0.039	0.073
wR_2[b]	0.101	0.074	0.141

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)^2]]^{0.5}$.

Calcd (found) for $C_{76}H_{79}BO_4P_2Ru$: C, 74.20 (74.02); H, 6.47 (6.77); Ru, 8.22 (7.95). IR (KBr, cm^{-1}): ν(C=C) 1641 (m). $^{31}P\{^1H\}$ NMR (32.44 MHz, CH$_2$Cl$_2$, −30 °C): δ 33.8 (s). $^{13}C\{^1H\}$ NMR (20.15 MHz, CDCl$_3$, 22 °C): δ 352.9 (t, $^2J_{PC}$ = 15.0 Hz, Ru=C), 164.4 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BPh$_4$), 136.3−121.4 (m, C−Ph), 115.2 (s, *C*HC$_6$H$_5$), 104.2 (s, *C*$_5$Me$_5$), 99.1 (s, CH), 66.7 (s, O*C*H$_2$CH$_2$), 36.8 (m, J = 34.1 Hz,[8] PCH$_2$), 24.8 (s, OCH$_2$*C*H$_2$), 10.1 (s, C$_5$*Me*$_5$). ^1H NMR (80.13 MHz, CDCl$_3$, 22 °C): δ 7.59−6.77 (m, 45 H, Ph), 5.49 (t, $^4J_{PH}$ = 2.0 Hz, 1H, CHPh), 3.84−0.86 (m, 18 H, alkanes), 1.44 (s, 15 H, Cp*).

Bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-*P*](pentamethylcyclopentadienyl)(η^1-*N*-diphenyldiazomethane)ruthenium(II) Tetraphenylborate (8). A solution of 1 (500 mg, 0.44 mmol) in 20 mL of dichloromethane was treated at −78 °C with a solution of 194 mg (1.00 mmol) of diphenyldiazomethane in 5 mL of dichloromethane. Upon warming of the solution to room temperature, the color changed from dark red to dark green. After the solution was stirred for approximately 30 min at ambient temperature, the solvent was removed under vacuum. The solid residue was washed several times with each 10 mL of *n*-pentane to separate excess diphenyldiazomethane. The dark green precipitate was collected by filtration (G3), washed with *n*-pentane, and evaporated to dryness: Yield 583 mg (95%) of the crude product; mp 85−86 °C dec; MS (FD, 60 °C) *m/e* 1002 [M$^+$ − BPh$_4$]. Anal. Calcd (found) for $C_{81}H_{83}BN_2O_4P_2Ru$: C, 73.57 (73.79); H, 6.33 (6.36); N, 2.12 (2.13), Ru, 7.64 (7.66). $^{31}P\{^1H\}$ NMR (32.44 MHz, CH$_2$Cl$_2$, −30 °C): δ 31.9 (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD$_2$Cl$_2$, 22 °C): δ 164.8 (q, $^1J_{CB}$ = 49.6 Hz, *ipso*-C of BPh$_4$), 160.3 (s, *ipso*-C of Ph$_2$CN$_2$), 136.4−122.2 (m, C−Ph), 100.3 (s, CH), 97.0 (s, *C*$_5$Me$_5$), 77.6 (s, Ph$_2$*C*N$_2$), 67.5 (s, O*C*H$_2$CH$_2$), 36.5 (m, J = 31.2 Hz,[8] PCH$_2$), 25.6 (s, OCH$_2$*C*H$_2$), 10.1 (s, C$_5$*Me*$_5$).

Crystallographic Analyses. Single crystals were obtained by slow diffusion of diethyl ether into concentrated CH$_2$Cl$_2$ solutions of **3**, **4**, and **6**, respectively. All crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo Kα radiation. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters and specific data collection parameters for **3**, **4**, and **6**, respectively, 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 **3**, **4**, and **6**, were 1.2, 1.6, and 1.0°, respectively. All structures were solved by Patterson methods[9] and refined by least squares with anisotropic thermal parameters for all nonhydrogen atoms. The use of a split model did not improve a further refinement of the large anisotropic thermal parameters observed for O(1) and O(2) in compound **3**. Hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 0.97 and −0.85 (**3**), 0.82 and −0.62 (**4**), and 1.14 and −1.66 eÅ^{-3} (**6**), respectively. The asymmetric unit of compounds **3** and **4** contains two solvent molecules of CH$_2$Cl$_2$. Final atomic coordinates are collected in Tables 2−4.

Results and Discussion

We are interested in transition metal complexes containing monodentate ($P{\sim}O$) and bidentate ($P^\frown O$) ether−phosphines. In complexes with such "hemilabile" ligands the coordinated oxygen can dissociate from the metal in solution, leaving a vacant coordination site, thus enabling to bind substrates.[10] On coordination of the oxygen to the metal, a chelate is formed. The dissociation and association of the weak donor leads to an "opening and closing mechanism". In complexes with two or three "hemilabile" ether−phosphine ligands the oxygen donors compete for one coordination site. This reveals a fluxional behavior in solution that has been studied by variable-temperature ^{31}P NMR spectroscopy.[4,11] As a result of the thermodynamic data based on line shape analyses the Ru−O bond in (ether−phosphine)(pentamethylcyclopentadienyl)ruthenium(II) complexes is determined to be rather weak if the (1,3-dioxan-2-ylmethyl)diphenylphosphine ligand is used.[4] This fact encouraged us to employ the synthetically and structurally described complex [Cp*Ru($P{\sim}O$)($P^\frown O$)][BPh$_4$] (**1**)[4] as a synthetic entry for the coordination of an extensive array of small molecules to the Cp*Ru fragment (Scheme 1). The ease of substrate binding depends on the coordinating abilities and the size of the incoming molecule, competing with the strength of the Ru−O bond.

Reactivity of 1 toward Olefins and Hydrogenations. An appropriate example for the "hemilabile" behavior of the employed O,P ligand is the reversibility of the reaction between **1** and ethene. Treatment of **1** with C$_2$H$_4$ in dichloromethane at room temperature leads to the ready cleavage of the Ru−O contact resulting in the quantitative formation of the corresponding η^2-ethene complex **2** (Scheme 1). The ethene addition was monitored by a color change of the solution from dark red to yellow. The η^2-coordination of the alkene to the ruthenium was proved by spectroscopic means. The $^{13}C\{^1H\}$ NMR spectrum of **2** displays a single resonance at 46.9 ppm which is assigned to the carbon atoms of the ethene ligand. In the $^{31}P\{^1H\}$ NMR spectrum of **2** two phosphorus resonances appear at −50 °C. When the temperature is raised the two resonances begin to broaden, then coalesce with final averaging to the expected singlet. This behavior is most consistent with a restricted Ru−P rotation because the $^{13}C\{^1H\}$ NMR spectrum (20.15 MHz) of **2** recorded at −80 °C shows broad signals for all carbon atoms of the ether−phosphine ligands. However, no decoalescence phenomena were revealed in the Cp* or ethene subspectra at this temperature indicating that rotation about the

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Table 2. Atomic Coordinates ($\times 10^4$, Esd's in Parentheses) of 3 with Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$)[a]

atom	*x*	*y*	*z*	U_{eq}
Ru(1)	2067(1)	1454(1)	1277(1)	17(1)
P(1)	1732(1)	2799(1)	1330(1)	19(1)
P(2)	2137(1)	1211(1)	1885(1)	19(1)
S	4303(1)	1538(1)	1283(1)	25(1)
O(1)	5204(5)	1894(5)	1530(1)	103(3)
O(2)	5027(5)	1213(4)	1014(2)	95(2)
O(3)	2134(4)	4443(2)	663(1)	33(1)
O(4)	4053(4)	4357(2)	1068(1)	29(1)
O(5)	4962(4)	1123(2)	2603(1)	30(1)
O(6)	3740(4)	2237(2)	2710(1)	29(1)
C(25)	−970(5)	2815(3)	1524(1)	32(1)
C(26)	−2326(6)	3065(3)	1518(2)	43(1)
C(27)	−2831(6)	3594(4)	1272(2)	51(2)
C(28)	−1963(6)	3882(3)	1041(2)	45(2)
C(29)	−582(5)	3660(3)	1048(1)	33(1)
C(30)	−65(5)	3116(3)	1290(1)	25(1)
C(31)	3892(5)	3444(3)	1758(1)	32(1)
C(32)	4492(7)	3858(3)	2031(2)	45(2)
C(33)	3663(8)	4200(3)	2261(2)	50(2)
C(34)	2243(8)	4136(3)	2213(1)	46(2)
C(35)	1625(6)	3711(3)	1933(1)	32(1)
C(36)	2461(5)	3355(2)	1707(1)	23(1)
C(37)	2561(6)	3288(3)	980(1)	26(1)
C(38)	2646(5)	4161(3)	990(1)	25(1)
C(39)	2173(6)	5267(3)	663(2)	41(1)
C(40)	3644(6)	5552(3)	760(2)	41(1)
C(41)	4191(6)	5176(3)	1096(2)	38(1)
C(42)	513(5)	2037(3)	2336(1)	24(1)
C(43)	−726(6)	2205(3)	2479(1)	34(1)
C(44)	−1897(6)	1766(3)	2398(1)	36(1)
C(45)	−1841(6)	1160(3)	2173(2)	36(1)
C(46)	−630(5)	984(3)	2026(1)	27(1)
C(47)	566(5)	1424(3)	2103(1)	21(1)
C(48)	1902(5)	−147(3)	2282(1)	28(1)
C(49)	2286(6)	−893(3)	2379(1)	34(1)
C(50)	3249(6)	−1278(3)	2206(1)	36(1)
C(51)	3886(6)	−937(3)	1944(1)	33(1)
C(52)	3524(5)	−190(3)	1846(1)	30(1)
C(53)	2514(5)	208(3)	2012(1)	21(1)
C(54)	3529(5)	1704(3)	2149(1)	26(1)
C(55)	3702(5)	1523(3)	2535(1)	22(1)
C(56)	3888(6)	2120(3)	3080(1)	33(1)
C(57)	5202(6)	1685(3)	3175(1)	31(1)
C(58)	5217(6)	955(3)	2966(1)	35(1)
C(59)	2025(5)	427(3)	914(1)	24(1)
C(60)	1839(5)	1113(3)	710(1)	25(1)
C(61)	562(5)	1446(3)	786(1)	27(1)
C(62)	−18(5)	996(3)	1051(1)	25(1)
C(63)	889(5)	357(3)	1122(1)	23(1)
C(64)	3101(6)	−170(3)	869(2)	40(1)
C(65)	2685(6)	1340(3)	422(1)	41(1)
C(66)	−202(7)	2050(3)	574(2)	44(2)
C(67)	−1498(5)	1043(3)	1140(2)	38(1)
C(68)	551(6)	−352(3)	1319(1)	31(1)
B(1)	6772(6)	8154(3)	773(1)	24(1)
C(1)	8209(6)	7295(3)	338(1)	32(1)
C(2)	8672(7)	6598(3)	215(2)	46(2)
C(3)	8327(7)	5926(3)	373(2)	51(2)
C(4)	7492(7)	5954(3)	643(2)	49(2)
C(5)	7062(6)	6642(3)	762(2)	41(1)
C(6)	7390(5)	7350(3)	615(1)	24(1)
C(7)	8589(5)	7884(3)	1326(1)	28(1)
C(8)	9177(6)	8044(3)	1657(1)	36(1)
C(9)	8641(6)	8605(3)	1854(1)	35(1)
C(10)	7515(6)	9030(3)	1710(1)	32(1)
C(11)	6961(5)	8880(3)	1378(1)	28(1)
C(12)	7447(5)	8291(3)	1172(1)	23(1)
C(13)	8626(5)	9081(3)	525(1)	28(1)
C(14)	9057(6)	9729(3)	360(1)	33(1)
C(15)	8099(6)	10257(3)	223(1)	35(1)
C(16)	6710(7)	10128(3)	257(1)	38(1)
C(17)	6289(6)	9468(3)	422(1)	29(1)
C(18)	7218(5)	8913(3)	559(1)	22(1)
C(19)	4313(5)	7892(3)	1043(1)	27(1)
C(20)	2884(6)	7725(3)	1016(2)	36(1)
C(21)	2184(6)	7675(3)	693(2)	42(1)
C(22)	2883(6)	7800(3)	402(2)	41(1)
C(23)	4302(6)	7970(3)	434(1)	32(1)
C(24)	5068(5)	8027(3)	755(1)	25(1)
C(70)	4991(9)	3542(5)	183(2)	80(2)
Cl(1)	6266(4)	4233(2)	168(1)	121(1)
Cl(2)	5505(2)	2767(1)	452(1)	68(1)
Cl(3)	11107(2)	6075(2)	1609(1)	96(1)
Cl(4)	8687(3)	5238(1)	1814(1)	100(1)
C(71)	9458(10)	5756(7)	1514(3)	113(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic Coordinates ($\times 10^4$, Esd's in Parentheses) of 4 with Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$)[a]

atom	*x*	*y*	*z*	U_{eq}
Ru(1)	1946(1)	1438(1)	1289(1)	14(1)
P(1)	1665(1)	2774(1)	1328(1)	17(1)
P(2)	2037(1)	1182(1)	1893(1)	17(1)
C(70)	3804(4)	1538(3)	1323(1)	21(1)
S(1)	5373(1)	1533(1)	1302(1)	37(1)
O(1)	2102(3)	4428(2)	658(1)	31(1)
O(2)	3991(3)	4300(2)	1060(1)	28(1)
O(3)	4925(3)	1116(2)	2590(1)	28(1)
O(4)	3677(3)	2203(2)	2716(1)	28(1)
C(25)	−1963(5)	3865(3)	1043(1)	39(1)
C(26)	−611(4)	3645(3)	1051(1)	29(1)
C(27)	−2814(4)	3580(3)	1280(1)	35(1)
C(28)	−2313(4)	3049(3)	1531(1)	32(1)
C(29)	−960(4)	2811(3)	1537(1)	26(1)
C(30)	−101(4)	3108(2)	1297(1)	21(1)
C(31)	1672(4)	3703(2)	1936(1)	25(1)
C(32)	2330(5)	4116(3)	2212(1)	34(1)
C(33)	3733(5)	4147(3)	2257(1)	34(1)
C(34)	4499(4)	3776(3)	2021(1)	30(1)
C(35)	3857(4)	3365(3)	1747(1)	25(1)
C(36)	2437(4)	3317(2)	1702(1)	21(1)
C(37)	2462(4)	3250(3)	970(1)	26(1)
C(38)	2601(4)	4123(3)	985(1)	24(1)
C(39)	4149(5)	5122(3)	1092(1)	37(1)
C(40)	3638(5)	5517(3)	764(1)	40(1)
C(41)	2172(5)	5256(3)	666(1)	40(1)
C(42)	3483(4)	−194(3)	1852(1)	26(1)
C(43)	3882(4)	−928(3)	1949(1)	31(1)
C(44)	3272(4)	−1305(3)	2208(1)	33(1)
C(45)	2242(5)	−947(3)	2374(1)	33(1)
C(46)	1848(4)	−203(3)	2281(1)	25(1)
C(47)	2451(4)	183(2)	2016(1)	20(1)
C(48)	−671(4)	957(3)	2025(1)	24(1)
C(49)	−1883(4)	1126(3)	2169(1)	31(1)
C(50)	−1947(4)	1721(3)	2408(1)	32(1)
C(51)	−780(4)	2138(3)	2503(1)	30(1)
C(52)	456(4)	1972(3)	2362(1)	24(1)
C(53)	501(4)	1377(3)	2119(1)	19(1)
C(54)	3424(4)	1685(2)	2147(1)	23(1)
C(55)	3655(4)	1493(3)	2535(1)	21(1)
C(56)	3873(5)	2075(3)	3090(1)	31(1)
C(57)	5193(5)	1662(3)	3171(1)	31(1)
C(58)	5227(5)	940(3)	2955(1)	32(1)
C(59)	−51(4)	923(3)	1024(1)	21(1)
C(60)	550(4)	1404(3)	777(1)	22(1)
C(61)	1858(4)	1104(3)	717(1)	20(1)
C(62)	2055(4)	413(2)	921(1)	21(1)
C(63)	887(4)	305(2)	1112(1)	20(1)
C(64)	−1507(4)	963(3)	1107(1)	30(1)
C(65)	−211(5)	2008(3)	562(1)	38(1)
C(66)	2765(4)	1373(3)	450(1)	32(1)
C(67)	3196(5)	−140(3)	894(1)	33(1)
C(68)	579(4)	−414(2)	1303(1)	25(1)
B(1)	3266(5)	3151(3)	4231(1)	21(1)
C(1)	1846(5)	2281(3)	4670(1)	34(1)
C(2)	1404(5)	1584(3)	4787(1)	45(1)
C(3)	1750(6)	899(3)	4630(2)	51(2)
C(4)	2568(6)	939(3)	4356(2)	49(2)
C(5)	3020(5)	1641(3)	4243(1)	39(1)
C(6)	2672(4)	2340(3)	4390(1)	23(1)
C(7)	5696(4)	2979(3)	4569(1)	30(1)
C(8)	7083(5)	2816(3)	4598(1)	39(1)
C(9)	7778(5)	2687(3)	4305(2)	41(1)
C(10)	7049(4)	2720(3)	3981(1)	36(1)
C(11)	5662(4)	2893(3)	3957(1)	26(1)
C(12)	4931(4)	3030(2)	4245(1)	22(1)
C(13)	1463(4)	2871(3)	3682(1)	27(1)
C(14)	861(4)	3011(3)	3348(1)	33(1)
C(15)	1391(4)	3576(3)	3140(1)	36(1)
C(16)	2486(4)	4003(3)	3278(1)	31(1)
C(17)	3073(4)	3865(3)	3614(1)	24(1)
C(18)	2588(4)	3279(2)	3828(1)	21(1)
C(19)	3747(4)	4478(3)	4584(1)	23(1)
C(20)	3327(5)	5128(3)	4751(1)	34(1)
C(21)	1969(5)	5250(3)	4796(1)	31(1)
C(22)	1022(4)	4720(3)	4656(1)	29(1)
C(23)	1441(4)	4076(3)	4483(1)	25(1)
C(24)	2838(4)	3915(2)	4445(1)	19(1)
C(71)	4970(7)	3515(4)	190(2)	70(2)
Cl(1)	6212(3)	4228(1)	170(1)	112(1)
Cl(2)	5555(2)	2757(1)	468(1)	58(1)
C(72)	−503(8)	5746(5)	1504(2)	99(3)
Cl(3)	1127(2)	6061(1)	1604(1)	92(1)
Cl(4)	−1245(2)	5232(1)	1819(1)	93(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic Coordinates ($\times 10^4$, Esd's in Parentheses) of 6 with Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)[a]

atom	x	y	z	U_{eq}
Ru(1)	2422(1)	1524(1)	846(1)	48(1)
P(1)	2254(2)	3081(2)	311(1)	48(1)
P(2)	1473(2)	1887(2)	1191(2)	52(1)
O(1)	1983(5)	1070(5)	−47(3)	56(2)
O(2)	1645(4)	590(5)	314(4)	56(2)
O(3)	605(4)	3607(6)	−1364(3)	53(2)
O(4)	1361(4)	4782(6)	−695(3)	54(2)
O(5)	22(5)	1206(6)	1421(4)	63(2)
O(6)	339(4)	−445(6)	1493(3)	55(2)
B(1)	6384(8)	2355(10)	1284(6)	50(4)
C(1)	7016(8)	2778(9)	496(6)	63(4)
C(2)	7011(9)	3000(9)	−80(7)	73(4)
C(3)	6365(11)	3018(9)	−589(7)	76(5)
C(4)	5727(9)	2850(9)	−517(7)	71(4)
C(5)	5747(8)	2612(8)	56(6)	60(4)
C(6)	6378(8)	2597(8)	597(6)	52(3)
C(7)	7600(8)	3212(10)	2110(6)	76(4)
C(8)	8305(8)	3216(10)	2532(7)	74(4)
C(9)	8686(8)	2358(11)	2701(6)	72(4)
C(10)	8380(8)	1492(12)	2416(6)	70(4)
C(11)	7656(8)	1487(9)	1975(6)	61(4)
C(12)	7240(7)	2357(10)	1808(6)	55(3)
C(13)	5470(7)	3927(9)	1096(6)	56(4)
C(14)	5072(7)	4653(9)	1267(7)	64(4)
C(15)	5145(8)	4667(10)	1889(8)	73(4)
C(16)	5606(7)	3980(10)	2317(7)	64(4)
C(17)	5981(7)	3288(8)	2109(5)	53(3)
C(18)	5950(7)	3215(9)	1509(5)	52(3)
C(19)	5868(7)	603(8)	786(6)	63(4)
C(20)	5569(7)	−329(9)	806(6)	66(4)
C(21)	5424(8)	−641(9)	1312(6)	63(4)
C(22)	5585(7)	−29(9)	1802(6)	60(4)
C(23)	5877(7)	918(9)	1789(6)	59(4)
C(24)	6029(6)	1259(8)	1291(5)	45(3)
C(25)	1750(8)	4650(9)	796(5)	55(4)
C(26)	1845(9)	5402(10)	1228(6)	68(4)
C(27)	2545(10)	5716(10)	1599(6)	71(4)
C(28)	3152(7)	5262(10)	1565(6)	59(4)
C(29)	3080(8)	4517(8)	1168(5)	49(3)
C(30)	2368(9)	4196(8)	773(6)	55(3)
C(31)	3000(6)	2500(9)	−421(5)	49(3)
C(32)	3391(8)	2661(11)	−800(6)	66(4)
C(33)	3618(7)	3601(11)	−861(6)	68(4)
C(34)	3485(8)	4379(10)	−559(6)	66(4)
C(35)	3100(7)	4229(9)	−185(5)	53(4)
C(36)	2850(6)	3276(9)	−111(5)	47(3)
C(37)	1361(5)	3151(7)	−331(4)	42(3)
C(38)	1313(7)	3788(8)	−884(5)	47(3)
C(39)	1318(7)	5440(9)	−1198(5)	61(4)
C(40)	614(7)	5253(10)	−1758(5)	68(4)
C(41)	535(7)	4172(9)	−1911(5)	60(4)
C(42)	308(8)	3227(11)	725(7)	75(4)
C(43)	−389(9)	3490(12)	302(7)	83(4)
C(44)	−759(9)	2929(13)	−210(7)	82(5)
C(45)	−459(9)	2086(12)	−322(7)	84(5)
C(46)	238(7)	1831(9)	99(6)	56(4)
C(47)	606(6)	2340(9)	624(5)	44(3)
C(48)	1300(8)	2576(9)	2254(6)	70(4)
C(49)	1481(8)	3107(10)	2799(7)	75(5)
C(50)	2087(8)	3712(9)	2980(6)	63(4)
C(51)	2479(7)	3794(9)	2614(6)	55(4)
C(52)	2286(8)	3290(9)	2080(6)	63(4)
C(53)	1682(8)	2653(9)	1869(5)	47(3)
C(54)	1204(7)	696(8)	1414(5)	56(4)
C(55)	367(8)	454(8)	1210(6)	61(4)
C(56)	−762(6)	1013(10)	1198(6)	72(4)
C(57)	−855(7)	38(10)	1451(6)	67(4)
C(58)	−434(7)	−742(10)	1280(6)	65(4)
C(59)	3016(6)	115(9)	1333(6)	48(3)
C(60)	3332(7)	494(9)	929(6)	54(4)
C(61)	3640(6)	1450(9)	1158(5)	47(3)
C(62)	3475(7)	1672(9)	1682(6)	50(3)
C(63)	3099(7)	845(9)	1774(6)	47(3)
C(64)	2686(7)	−881(8)	1275(5)	59(4)
C(65)	3415(7)	−60(8)	407(5)	71(4)
C(66)	4177(6)	2038(9)	972(6)	67(4)
C(67)	3851(7)	2474(9)	2147(5)	64(4)
C(68)	2953(6)	688(8)	2358(5)	55(3)

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

ruthenium−Cp* bond axis and rotation about Ru−ethene remain rapid. The origin of this effect is reasonably due to steric reasons, because it is only observable if a bulky ancillary ligand such as ethene in the present case or chlorine[4] is coordinated to the $Cp^*Ru(P{\sim}O)_2$ fragment. This is in agreement with a recent study describing the restricted Cr−P rotation in complexes of the type $(\eta^6\text{-}C_6R_6)Cr(CO)_2(PPh_3)$ as the process of highest energy.[12] The barrier of the Ru−P rotation $\Delta G_c^{\ddagger}$ was estimated from the variable-temperature ^{31}P NMR spectroscopic data, using the approximate equation: $\Delta G_c^{\ddagger} = RT_c\,(22.96 + \ln T_c/\delta\nu)$.[13] The obtained values are as follows: $T_c = 248$ K; $\Delta G_{248}^{\ddagger} = 48.1$ kJ/mol^{-1}.

In contrast to the reported cyclopentadienylruthenium η^2-ethene complexes provided with PMe_3[14] and PPh_3[15] ligands, respectively, this reaction is fully reversible. If **2** is stirred under an atmosphere of argon, the color of the solution turns to dark red again resulting in the quantitative formation of the educt **1** which was identified by $^{31}P\{^1H\}$ NMR spectroscopy. Attempts to isolate **2** by precipitation from an ethene saturated CH_2Cl_2 solution with diethyl ether failed. Again **1** was found as a precipitate. If **1** is reacted with styrene and 1-hexene under the same conditions the corresponding η^2-coordinated olefin complexes are not observed. However, stable η^2-styrene complexes containing the $CpRu(PPh_3)_2$[15] and $CpRu(PMe_3)_2$[16] moieties, respectively, were reported in the literature. These differences in the reactivity of **1** toward higher olefins can possibly be traced back to the steric demand of the Cp* ring, but also an influence of the ether arm may not be excluded.

The weak and hence reversible η^2-ethene coordination in **2** encouraged us to study the potential catalytic activity of **1** toward the hydrogenation of olefins. The results of the hydrogenation experiments are listed in Table 5. Complex **1** is able to hydrogenate 1-hexene to *n*-hexane at moderate pressures, but elevated temperatures (>80 °C) and long reaction times (4 h) are required to achieve an acceptable rate of conversion. Due to the poor solubility of **1** in 1-hexene the hydrogenation reactions in THF are more effective compared to experiments without any solvent. This is nicely reflected by the different conversion rates at 100 °C (see Table 5).

Reaction of 1 with Sulfur Dioxide. If sulfur dioxide is bubbled into a solution of **1** in dichloromethane at room temperature, a spontaneous color change from dark red to orange occurred. The formation of the SO_2 complex **3** (Scheme 1) is quantitative after approximately 5 min. This is indicated by a singlet in the $^{31}P\{^1H\}$ NMR spectrum at 23.5 ppm. Complex **3** is an air-stable yellow compound which is readily soluble in dichloromethane but is insoluble in nonpolar solvents. The $^{13}C\{^1H\}$ NMR and the IR spectroscopic data of **3** are well comparable to that of the related $[Cp^*Ru(PPh_3)_2(SO_2)][PF_6]$ complex.[17] The two SO_2 stretching

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Scheme 1

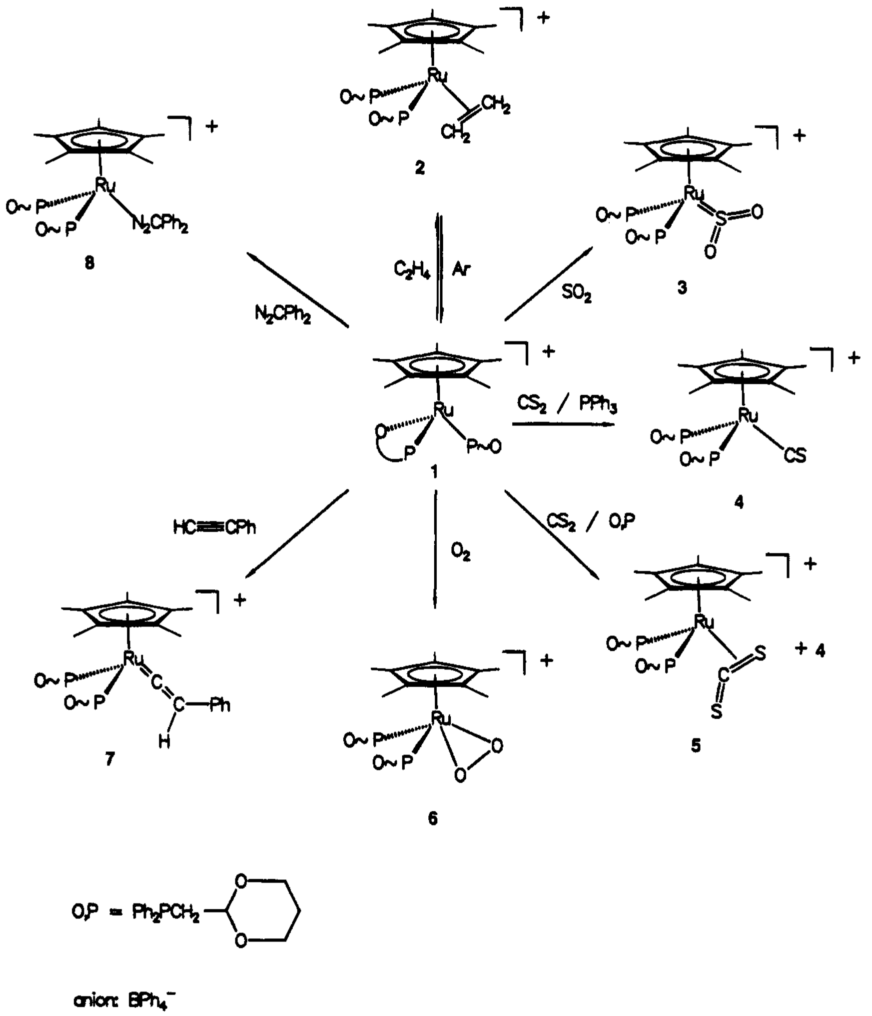

Table 5. Catalytic Hydrogenation of 1-Hexene to *n*-Hexane with 1[a]

T, °C	*p*, bar	time, h	conversion, %
80	50	4	42
100	50	4	99
100[b]	50	4	50

[a] All reactions were accomplished using a molar ratio of 1-hexene:catalyst = 10^3:1 and an initial amount of 50 mg of 1; solvent, 10 mL of THF. [b] Without solvent.

frequencies at 1277 and 1109 cm^{-1} are in the typical range reported for the η^1-coplanar SO_2 geometry.[18] The fact that complex **3** is not able to undergo a sulfate formation with dioxygen but slowly converts to the dioxygen species **6** provides further proof for the presence of a coplanar $RuSO_2$ moiety.[18]

The structure of complex **3** was determined by an X-ray crystal structure analysis to ensure the mode of SO_2 coordination. The ORTEP drawing of the cation of **3** is shown in Figure 1. Table 6 contains selected bond distances and angles. The geometry of **3** is octahedral about the metal center, with the Cp* ligand occupying three coordination sites. This is evidenced by the near 90° bond angles between P(1)–Ru(1)–P(2), P(1)–Ru(1)–S, and P(2)–Ru(1)–S, respectively. The large anisotropic thermal parameters observed for O(1) and O(2) are obviously due (see Experimental Section) to a thermal motion of the SO_2 ligand, which cannot be frozen at −100 °C. The ruthenium–sulfur distance is 2.133(2) Å, which is close to the range usually reported for the coplanar geometry[18] and nearly equivalent to that found for $CpRu(PPh_3)(SO_2)(S(SO_2)R)$[19] (Ru–S = 2.121(3) Å). The $RuSO_2$ fragment consists of a plane which is perpendicular to that of the Cp* ligand, like in $[CpFe(CO)_2(SO_2)][AsF_6]$.[20]

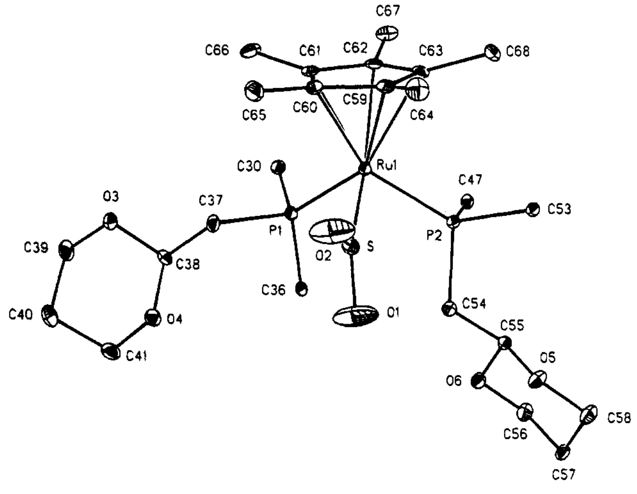

Figure 1. ORTEP plot of the cation of **3**. The phenyl groups were omitted for clear view.

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Table 6. Selected Interatomic Distances (Å) and Angles (deg) for 3

Bond Lengths			
Ru(1)−P(1)	2.346(2)	S−O(1)	1.368(5)
Ru(1)−P(2)	2.359(2)	S−O(2)	1.403(5)
Ru(1)−S	2.133(2)		
Bond Angles			
P(1)−Ru(1)−P(2)	94.67(4)	Ru(1)−S−O(1)	127.4(2)
P(1)−Ru(1)−S	94.31(5)	Ru(1)−S−O(2)	121.0(2)
P(2)−Ru(1)−S	93.05(7)	O(1)−S−O(2)	111.6(3)

Reaction of 1 with Carbon Disulfide. Treatment of 1 with a threefold excess of PPh_3 and carbon disulfide in dichloromethane at ambient temperature immediately results in the development of a dark purple color of the reaction mixture. However, for a complete reaction several hours are required. This was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After the solution was stirred overnight the purple color faded to orange-brown and the quantitative conversion of 1 was indicated in the $^{31}P\{^1H\}$ NMR spectrum. Separation of excess PPh_3 and $SPPh_3$ via column chromatography leads to an orange-brown crude product containing the thiocarbonyl complex 4 (Scheme 1) together with mixed phosphine η^2-CS_2 ruthenium complexes. We were able to isolate 4 in a pure form by crystallization from a diethyl ether/CH_2Cl_2 mixture yielding bright yellow air-stable crystals which are soluble in dichloromethane but are insoluble in nonpolar solvents. To the best of our knowledge complex 4 represents the first thiocarbonyl species containing the Cp or Cp* bis(phosphine)ruthenium fragment. Its $^{31}P\{^1H\}$ NMR spectrum displays a single resonance at 29.2 ppm. The IR spectrum exhibits one band at 1264 cm^{-1} in the thiocarbonyl region which is shifted approximately 100 cm^{-1} toward lower energy compared to the related complex $[CpRu(CO)_2(CS)]^+$.[21] This indicates the high electron density at the ruthenium center in 4. Although many thiocarbonyl complexes are cited in the literature,[22] only a few ^{13}C chemical shift data of the thiocarbonyl group are reported. Due to the coupling with two equivalent P atoms the $^{13}C\{^1H\}$ NMR spectrum of 4 reveals a low-intensity triplet at very low field (314 ppm) which is assigned to the carbon atom of the CS ligand. This value is well comparable to that reported for the thiocarbonyl moiety of *mer,trans*-$Cr(CO)_3(CS)[P(OPh)_3]_2$.[23]

An ORTEP plot of the molecular structure of 4 is shown in Figure 2. A listing of selected bond distances and angles is given in Table 7. Complex 4 is again octahedrally coordinated about the ruthenium center which is shown by the near 90° bond angles between P(1)−Ru(1)−P(2), P(1)−Ru(1)−C(70), and P(2)−Ru(1)−C(70), respectively. The ruthenium−carbon bond length (Ru(1)−C(70) = 1.832(4) Å) corresponds to the Cr−C distance in *mer,trans*-$Cr(CO)_3(CS)[P(OPh)_3]_2$[23] (1.87(1) Å). This distance agrees well with that of the related η^1-vinylidene complex $[CpRu(C{=}CH_2)(PMe_2Ph)_2][BF_4]$[24] and is in the range of a typical ruthenium−carbon double bond. The Ru−C−S unit deviates from the expected linear geometry forming an angle of 170.9(3)°.

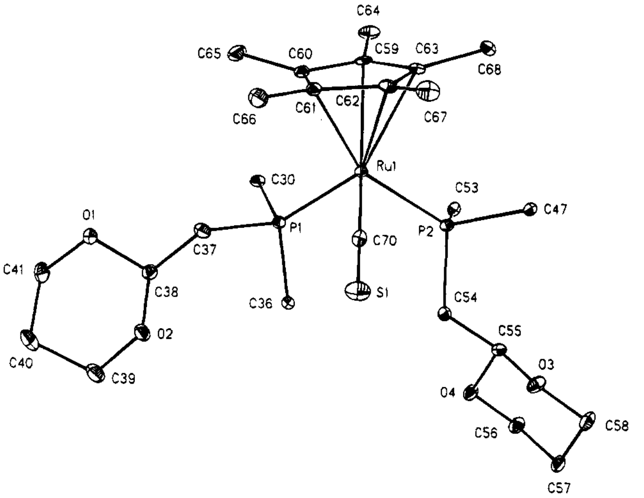
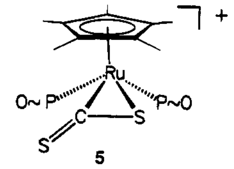


Figure 2. ORTEP presentation of the cation of 4. The phenyl groups were omitted for clearity.

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for 4

Bond Lengths			
Ru(1)−P(1)	2.343(1)	Ru(1)−C(70)	1.832(4)
Ru(1)−P(2)	2.357(1)	C(70)−S(1)	1.554(4)
Bond Angles			
P(1)−Ru(1)−P(2)	96.88(4)	P(2)−Ru(1)−C(70)	89.3(1)
P(1)−Ru(1)−C(70)	91.3(1)	Ru(1)−C(70)−S(1)	170.9(3)

If 1 was reacted with carbon disulfide in the absence of triphenylphosphine the CH_2Cl_2 solution slowly turned to dark brown after stirring overnight at ambient temperature. The formation of the η^2-CS_2 complex 5 was proved by a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. Unfortunately it was not possible to isolate 5 in a pure form. Thus, the isolation of the η^2-CS_2 species was successful by reacting 1 with a threefold excess of the O,P ligand and carbon disulfide in CH_2Cl_2 overnight at room temperature. Similar to the reaction of 1 with PPh_3/CS_2 a dark purple color occurred almost immediately and faded to orange-brown after prolonged stirring. The working up of the reaction mixture was carried out as described above to yield the complexes 4 and 5 (Scheme 1) without further side products. Pure 5 was obtained after separation of the thiocarbonyl complex 4 by crystallization from a diethyl ether/CH_2Cl_2 mixture in 61% yield. 4 is an air-stable orange-brown compound which is readily soluble in dichloromethane and acetone but is insoluble in nonpolar solvents. Its $^{31}P\{^1H\}$ NMR spectrum at −30 °C and even at room temperature displays two resonances at 39.7 and 4.8 ppm, indicating two diastereotopic phosphorus nuclei, which is caused by the absence of an intramolecular mirror plane in compound 5. This is traced back to the position of the η^2-coordinated CS_2 group, as depicted as follows:



5

A high barrier of rotation of the CS_2 fragment is assumed for that case. This is in contrast to the related complex $[CpRu(PPh_3)_2(CS_2)][HgCl_3]$[25] showing two equi-

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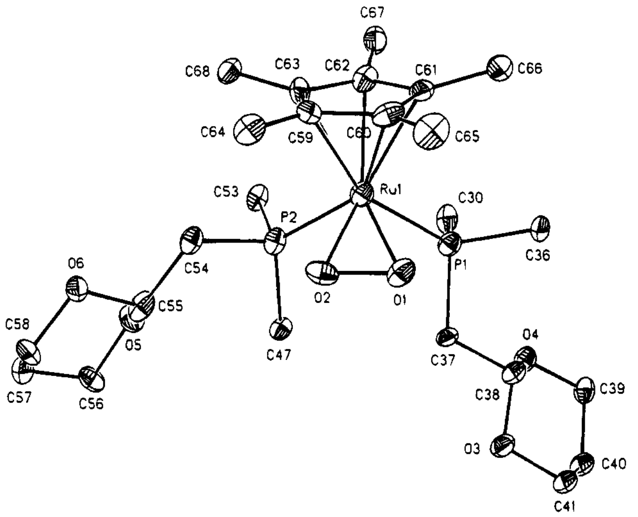

Figure 3. ORTEP plot of the cation of **6**. The phenyl groups were omitted for clear view.

Table 8. Selected Interatomic Distances (Å) and Angles (deg) for 6

Bond Lengths			
Ru(1)−P(1)	2.352(4)	Ru(1)−O(1)	1.970(8)
Ru(1)−P(2)	2.327(5)	Ru(1)−O(2)	1.958(7)
O(1)−O(2)	1.394(9)		
Bond Angles			
P(1)−Ru(1)−P(2)	91.8(1)	P(2)−Ru(1)−O(2)	79.7(3)
P(1)−Ru(1)−O(1)	79.2(2)	P(2)−Ru(1)−O(1)	109.7(3)
P(1)−Ru(1)−O(2)	108.3(3)	O(1)−Ru(1)−O(2)	41.6(3)

valent phosphines. The $^{13}C\{^1H\}$ NMR spectrum of **5** shows the carbon resonance of the CS_2 group as a low intensity doublet of doublets at about 201 ppm, because of the coupling with two inequivalent phosphorus atoms. The observed inequivalency of the two O,P ligands in **5** can also be demonstrated by the appearance of two sets of resonances for almost each carbon atom of the ether moiety. One strong IR absorption at 1266 cm^{-1} is observed for the η^2-bonded carbon disulfide. The second CS_2 absorption which should be in the range 820−860 cm^{-1} [25,26] cannot be assigned unequivocally.

Attempts to coordinate carbon dioxide to the Cp*Ru fragment failed even under elevated pressure (≈5 bar).

Reaction of 1 with Oxygen. A solution of **1** in dichloromethane readily takes up oxygen to give the dark yellow dioxygen complex **6** in quantitative yield (Scheme 1). Complex **6** forms an air-stable precipitate which is easily soluble in dichloromethane or acetone but is insoluble in nonpolar solvents. Its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 18.5 ppm. The $^{13}C\{^1H\}$ NMR data correspond well to those of the currently reported complex $[Cp^*Ru(dppe)(O_2)]^+$.[27] A solution of the oxygen complex in liquid SO_2 did not react to a sulfato species, but to some extent a conversion to the η^1-SO_2 complex **3** took place after a prolonged reaction time.

Figure 3 shows the molecular structure of the cation of **6**. Selected bond distances and angles are presented in Table 8. The structure of **6** is very similar to those of the corresponding complexes **3** and **4**. The compounds **3**, **4**, and **6** crystallize in the same monoclinic space group $P2_1/c$. The Ru−P distances as well as the conformation of the two O,P ligands are nearly equivalent. In all cases both O,P phenyl groups are directed away from the coordinated small molecule. In **6**, the dioxygen ligand is symmetrically bound to Ru with Ru−O distances of 1.970(8) and 1.958(7) Å, respectively, which are slightly shorter than that reported for $[Cp^*Ru(dppe)(O_2)]^+$.[27] The O(1)−O(2) bond length is 1.394(9) Å, which is approximately halfway between the reported superoxide and peroxide distances, being 1.28 and 1.49 Å, respectively.[28,29] The angle between the planes O(1)−Ru(1)−O(2) and P(1)−Ru(1)−P(2) was found to be 96.3°.

Reaction of 1 with Phenylacetylene. A series of η^1-vinylidene complexes has been generated by substitution of the chloride in $CpRuClL_2$ (L = tertiary phosphine) with various 1-alkynes.[30] These complexes are formed by a rapid alkyne to vinylidene rearrangement of an η^2-alkyne intermediate, which cannot be isolated in most of the cases. However, the use of small alkyne substituents and small ancillary ligands at the ruthenium has led to the synthesis of the η^2-ethyne complex $[CpRu(PMe_2Ph)(\eta^2\text{-}C_2H_2)][BF_4]$.[24] The interaction of phenylacetylene with **1** in dichloromethane at room temperature results in an instantaneous and quantitative formation of the η^1-vinylidene complex **7** (Scheme 1). No indication for the occurrence of an intermediary species was observed during the reaction. Complex **7** is an air-stable pale red compound which is easily soluble in dichloromethane or acetone but is insoluble in nonpolar solvents. Its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 33.8 ppm. The medium intensity absorption at 1641 cm^{-1} in the IR spectrum of **7** is assigned to the vinylidene C=C stretching frequency. The vinylidene ligand in **7** displays a ^1H NMR triplet ($\delta_H = 5.49$, $^4J_{PH} = 2.0$ Hz), a highly deshielded C_α triplet ($\delta_C = 352.9$, $^2J_{PC} = 15.0$ Hz), and a vinylic C_β singlet ($\delta_C = 115.2$), which is typical of phosphine substituted complexes of this type.[24,30]

Reaction of 1 with Diphenyldiazomethane. The reaction of **1** with an excess of diphenyldiazomethane in dichloromethane at −78 °C is accompanied by a color change to dark green upon warming to room temperature. The diphenyldiazomethane complex **8** (Scheme 1) is obtained in high yields as a dark green air-stable crude product which is soluble in dichloromethane but is insoluble in nonpolar solvents. The product is still contamined with a small amount of diphenyldiazomethane after workup (see Experimental Section). However, satisfactory elemental analyses could be obtained. A further purification by crystallization from diethyl ether/CH_2Cl_2 mixtures failed leading to the precipitation of the starting complex **1**. The $^{31}P\{^1H\}$ NMR spectrum of **8** displays a single resonance at 31.9 ppm. The $^{13}C\{^1H\}$ NMR data of the coordinated diphenyldiazomethane ligand are well comparable to that reported for the corresponding rhodium complex $RhCl(AsiPr_3)_2(N_2CPh_2)$.[31] The *ipso*-C atoms of the phenyl groups display a singlet at 160.3 ppm. The low-intensity resonance at 77.6 ppm is assigned to the carbene carbon atom. Attempts to prepare the η^2-dinitrogen species by irradiation of **8** with UV light in dichloromethane failed which is in marked contrast to the rhodium analogue. Even the treatment of **8** in

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boiling THF did not lead to a remarkable conversion. We note that on prolonged stirring of solutions of **1** under nitrogen (≈5 bar) no cleavage of the Ru−O contact by N_2 occurs.

Conclusion

Ether−phosphines belong to a special class of "hemilabile" ligands in which the phosphorus atom is strongly coordinated to the transition metal center while the ether oxygen atom forms only a weak contact in such a way that the ether moiety functions as an intramolecular solvent. An important role of the ether substituent is the protection of an undercoordinated and hence very reactive transition metal complex fragment. Complex **1**, which represents such an isolable intramolecular solvent complex, was anticipated to be a reactive precursor for the coordination of small molecules to the ruthenium center. The main topic of this work was the examination which substrates are suitable to cleave the weak Ru−O bond under mild conditions. As expected, complex **1** shows excellent reactivity toward phenylacetylene, sulfur dioxide, carbon disulfide, oxygen, and diphenyldiazomethane resulting in the irreversible addition of the corresponding molecule to the Cp*Ru fragment. However, the ability of the incoming substrate to bind to the metal is strongly influenced by its coordinating properties due to the "hemilabile" nature of the ether−phosphine ligands. This is nicely reflected by the reversibility of the reaction of **1** with ethene, which is in marked contrast to related systems provided with classical tertiary phosphines. Moreover, the acceptable catalytic activity of **1** toward the hydrogenation of 1-hexene to *n*-hexane is considered to be a successful application of the weak metal−olefin interaction.

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Supplementary Material Available: Tables of H coordinates and *U* values, anisotropic thermal parameters, crystal structure parameters, and interatomic distances and angles of **3**, **4**, and **6** (24 pages). Ordering information is given on any current masthead page.

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