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Behavior of the Bis(chelate) Complex $[Rh(\overset{\frown}{PO})_2][BPh_4]$ toward Acyl Halides and Carbon Monoxide. Investigation of a Reversible Alkyl Migration

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The bis(chelate) complex $[Rh(\overset{\frown}{PO})_2][BPh_4]$ (**2**; $\overset{\frown}{PO}$ = η^2(O,P)-chelated $(C_6H_{11})_2PCH_2CH_2OCH_3$ ligand) reacts with acyl chlorides RC(O)Cl to give the acyl complexes $[Rh(\overset{\frown}{PO})_2C(O)RCl][BPh_4]$ (**4a–e**; R = CH_3 (**a**), C_2H_5 (**b**), *i*-C_3H_7 (**c**), Ph (**d**), C_2H_4Ph (**e**)). The structure of **4c**, showing a distorted-octahedral configuration, was elucidated by an X-ray structural analysis. **4c** crystallizes in the monoclinic space group *P*2/*n* with *Z* = 4. The cell dimensions are *a* = 21.881(4) Å, *b* = 10.303(2) Å, *c* = 26.516(5) Å, and *β* = 100.91(3)°. The reductive-elimination process of **4a** proceeds via a reverse methyl migration to give **6a**, followed by elimination of CH_3Cl from **6a** to form the carbonylrhodium(I) complex $[Rh(CO)(P\sim O)(\overset{\frown}{PO})][BPh_4]$ (**8**; $P\sim O$ = η^1(P)-coordinated $(C_6H_{11})_2PCH_2CH_2OCH_3$ ligand). $[ClRh(P\sim O)_2(CO)]$ (**9**) is observed as the final product. Both Rh–O bonds in **2** are cleaved by 5-bar pressure of carbon monoxide, resulting in the formation of the tricarbonylrhodium(I) complex $[Rh(P\sim O)_2(CO)_3][BPh_4]$ (**3**). Upon bubbling argon through a CH_2Cl_2 solution of **3**, $[(OC)_2Rh(P\sim O)_2][BPh_4]$ (*cis*-**5** or *trans*-**7**) is favored compared to the monocarbonyl species **8**.

Introduction

Alkyl migration, in which carbon monoxide is involved, has been intensively studied because of its significance for the formation of carbon–carbon bonds in transition-metal-catalyzed processes.[1] Many aspects of this reaction, including the effects of stereochemistry,[2] solvents,[3] and incoming ligands[4] and the characterization of unsaturated intermediates formed upon migration, have been previously examined in great detail.

The introduction of hemilabile ether–phosphine ligands has been very successful in the cobalt-catalyzed hydrocarbonylation of methanol to acetaldehyde. Methanol conversions and selectivities to acetaldehyde rose to 90 and 85%, respectively.[5] To get an insight into the catalytic cycle, a rhodium-based model system has been recently established.[6,7]

This process is composed of three steps: oxidative addition of methyl iodide, methyl migration, and reductive elimination of acetyl iodide. The methyl migration which leads to the complexes $[cis\text{-}(\overset{\frown}{PO})_2Rh(C(O)CH_3)(I)][SbF_6]$ containing two Rh–O bonds [$\overset{\frown}{PO}$ = η^2(O,P)-coordinated PO ligand; $P\sim O$ = η^1(P)-coordinated PO ligand; PO = $R_2PCH_2\overline{CHCH_2CH_2CH_2O}$ (R = CH_3, *n*-C_3H_7), $R_2PCH_2CH_2OCH_3$ (R = *n*-C_3H_7, C_6H_5)] is promoted by ether–phosphines. Rhodium(III) is more oxophilic than rhodium(I); hence, bis(chelate) complexes are usually more preferred. In this way the ether moiety may be regarded as an intramolecular solvent to stabilize the final product.[8]

The present investigation demonstrates the dependence of the course of the reaction on the basicity of ether–phosphines. The oxidative addition of acetyl chloride to the bis(chelate) complex $[Rh(\overset{\frown}{PO})_2][BPh_4]$ (PO = $(C_6H_{11})_2PCH_2CH_2OCH_3$) and the reductive elimination from the acyl complexes which is subject to a reverse alkyl migration have been monitored by $^{31}P\{^1H\}$ NMR spectroscopy and GC–MS.

In order to investigate the reactivity of both Rh–O bonds, the bis(chelate) complex $[Rh(\overset{\frown}{PO})_2][BPh_4]$ was allowed to react with carbon monoxide.

Experimental Section

General Procedures. All operations were performed under dry, oxygen-free argon using the usual Schlenk techniques. Solvents were purified by standard methods and stored under argon. Instrumentation: mass spectra, Finnigan MAT 711 A (modified by AMD); GC–MS, Varian MAT 112 S; IR, Bruker FT-IR spectrometer, Model IFS 48; ^1H and $^{13}C\{^1H\}$ NMR, Bruker AC 80, Bruker AC 250, and Bruker Cryospec WM 400 at 80.13 and 20.15, 250.13 and 62.90, and 400.13 and 100.62 MHz, respectively; $^{31}P\{^1H\}$ NMR, Bruker WP 80 at 32.39 MHz, external standard at low temperatures (0 to −80 °C) 1% H_3PO_4 in acetone-d_6; GC, 6000 Vega Series 2 from Carlo Erba with FID and thin-film quartz capillary column SP 1000, 50 m, integrator 3393A from Hewlett-Packard. Elemental analyses were carried out with Carlo Erba Model 1106 and Perkin-Elmer Model 4000 atomic absorption spectrometers. The starting compounds $[(\mu\text{-}Cl)Rh(COE)_2]_2$ (**1**;[9] COE = cyclooctene) and $(C_6H_{11})_2PCH_2CH_2OCH_3$ (PO)[10] were prepared as described in the literature.

Bis[dicyclohexyl(methoxyethyl)phosphine-*O*,*P*]rhodium(I) Tetraphenylborate (2). To a solution of $[(\mu\text{-}Cl)Rh(COE)_2]_2$ (**1**; 72 mg, 0.1 mmol) in 10 mL of acetone were added 68.4 mg (0.2 mmol) of $NaBPh_4$ and 105 mg (0.4 mmol) of the ligand $(C_6H_{11})_2$-

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PCH$_2$CH$_2$OCH$_3$ (PO) in one portion, and the solution was allowed to react 10 min at 0 °C. The solvent was removed under reduced pressure to give an orange solid. The solid was cooled to −60 °C, and 5 mL of dichloromethane was added. NaCl was removed by filtration (P4), and 25 mL of *n*-hexane was added to the solution. The precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo to yield 30 mg (48.8%) of the crude product as a yellow solid, which is very air-sensitive. This product decomposes very quickly in solution and slowly in the solid state at −40 °C. MS (FD, 8 kV, 35 °C): *m/e* 615 $[Rh(P^\frown O)_2]^+$. Anal. Calcd for $C_{54}H_{78}BO_2P_2Rh$: C, 69.38; H, 8.41; Rh, 11.01. Found: C, 68.07;[11] H, 8.27; Rh, 11.61.

Tricarbonylbis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(I) Tetraphenylborate (3). A solution of 2 (30 mg, 0.05 mmol) in 5 mL of dichloromethane was stirred at −40 °C under an atmosphere of CO (5 bar) until a pale yellow solution was obtained. **3** is only stable under an atmosphere of carbon monoxide at −40 °C and cannot be isolated.

General Preparation of the Complexes 4a–e. A 0.3-mL (4.2-mmol) portion of acetyl chloride was added to a solution of **2** (30 mg, 0.05 mmol) in 5 mL of dichloromethane, and the mixture was allowed to react 60 min at 0 °C. The solvent was removed in vacuo. The crude product was dissolved in 2 mL of dichloromethane, and 50 mL of *n*-hexane was added to the solution. The yellow precipitate was collected by filtration (P4), washed three times with 2 mL of *n*-hexane, and dried in vacuo.

Acetylchlorobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]rhodium(I) Tetraphenylborate (4a). **4a** is unstable above 0 °C and is subject to methyl migration. MS (FAB, 35 °C): *m/e* 693 $[Rh(P^\frown O)_2(CH_3CO)Cl]^+$.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]propionylrhodium(I) Tetraphenylborate (4b). **4b** is unstable above 0 °C, and alkyl migration takes place. MS (FAB, 35 °C): *m/e* 707 $[Rh(P^\frown O)_2(C_2H_5CO)Cl]^+$.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]-(2-methylpropionyl)rhodium(I) Tetraphenylborate (4c). **4c** was isolated as a pure product and did not undergo alkyl migration; mp 60 °C dec. MS (FAB, 35 °C): *m/e* 721 $[Rh(P^\frown O)_2(C_3H_7CO)Cl]^+$. Anal. Calcd for $C_{58}H_{85}BClO_3P_2Rh$: C, 66.89; H, 8.23; Rh, 9.88. Found: C, 65.94;[11] H, 8.22; Rh, 9.00.

Benzoylchlorobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]rhodium(I) Tetraphenylborate (4d). **4d** can be isolated but slowly undergoes aryl migration; mp 100 °C dec. MS (FAB, 35 °C): *m/e* 755 $[Rh(P^\frown O)_2(C_6H_5CO)Cl]^+$. Anal. Calcd for $C_{61}H_{83}BClO_3P_2Rh$: C, 68.32; H, 7.52; Rh, 9.60. Found: C, 68.48; H, 8.15; Rh, 8.75.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]-(3-phenylpropionyl)rhodium(I) Tetraphenylborate (4e). **4e** can be isolated but slowly undergoes alkyl migration: mp 71 °C dec. MS (FAB, 35 °C): *m/e* 783 $[Rh(P^\frown O)_2(C_6H_5CH_2CH_2CO)Cl]^+$. Anal. Calcd for $C_{63}H_{87}BClO_3P_2Rh$: C, 68.57; H, 7.95; Rh, 9.33. Found: C, 67.25;[11] H, 8.21; Rh, 8.97.

Acetylbromobis[dicyclohexyl(methoxyethyl)phosphine-*O,P*]rhodium(I) Tetraphenylborate (4′a). The reaction between CH$_3$C(O)Br and **2** does not proceed quantitatively, and the product cannot be isolated in a pure form. MS (FD, 8 kV, 35 °C): *m/e* 739 $[Rh(P^\frown O)_2CH_3COBr]^+$.

***cis*-Dicarbonylbis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(I) Tetraphenylborate (5).** Argon was bubbled through a solution of **3** in 5 mL of dichloromethane (61 mg, 0.1 mmol) at −40 °C for approximately 30 min. The solvent was reduced to 2 mL. A 30-mL portion of *n*-hexane was added, and the crude product was obtained as a yellow solid. **5** is unstable and transforms slowly into **7** and cannot be isolated as a pure product.

***trans*-Dicarbonylbis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(I) Tetraphenylborate (7).** **7** was obtained by stirring a solution of **5** (67 mg, 0.1 mmol) in 5 mL of dichloromethane until only one CO absorption appeared in the IR. The rate of the transformation from **5** to **7** is temperature-dependent, and the whole process takes approximatively 30 min at −30 °C. The solvent was reduced to 2 mL. A 30-mL portion of *n*-hexane was added to the solution, and the crude product was obtained as a yellow solid. The conversion is quantitative. $^{13}C\{^1H\}$ NMR (62.90 MHz, CDCl$_3$, 303 K): δ 189.15 (dt, $^1J_{RhC}$ = 74.2, $^2J_{PC}$ = 15.3 Hz, CO). MS (FD, 8 kV, 35 °C): *m/e* 643 $[Rh(P{\sim}O)_2(CO)]^+$. Anal. Calcd for $C_{56}H_{78}BO_4P_2Rh$: C, 67.88; H, 7.93; Rh, 10.39. Found: C, 66.69;[11] H, 7.84; Rh, 10.90.

Carbonyl-*trans*-[dicyclohexyl(methoxyethyl)phosphine-*P*][dicyclohexyl(methoxyethyl)phosphine-*O,P*]rhodium(I) Tetraphenylborate (8). To a solution of **9** (68 mg, 0.1 mmol) in 5 mL of dichloromethane was added excess NaBPh$_4$ (35 mg, 1.0 mmol), and the solution was stirred at −20 °C for 12 h. The reaction was monitored until no **9** remained, as determined by IR spectroscopy. Excess NaBPh$_4$ and NaCl were removed by filtration (P4), and the solvent was reduced to 2 mL. A 30-mL portion of *n*-hexane was added, and the crude product of **8** and the dimer $[(\mu\text{-}CO)Rh(O,P)]_2$[12] were obtained as a pale yellow solid and dried in vacuo. MS (FD, 8 kV, 35 °C): *m/e* 643 $[Rh(P^\frown O)(P{\sim}O)CO]^+$. $^{31}P\{^1H\}$ NMR and IR data: see Table III.

Carbonylchloro-*trans*-bis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(I) (9). To a solution of **1** (72 mg, 0.1 mmol) in 5 mL of acetone was added 105 mg (0.4 mmol) of the ligand (C$_6$H$_{11}$)$_2$PCH$_2$CH$_2$OCH$_3$ (PO) in one portion. Carbon monoxide was passed through the solution until a pale yellow solution was obtained, and the solvent was removed in vacuo. The crude product was dissolved in dichloromethane (2 mL), and 50 mL of *n*-hexane was added to the solution. The yellow precipitate was collected by filtration (P4), washed three times with 2 mL of *n*-hexane, and dried in vacuo: yield 52 mg (76%); mp 100 °C. MS (FD, 8 kV, 35 °C): *m/e* 678 $[Rh(P{\sim}O)_2COCl]^+$. Anal. Calcd for $C_{31}H_{58}ClO_3P_2Rh$: C, 54.83; H, 8.61; Rh, 15.15. Found: C, 54.80; H, 9.05; Rh, 15.80.

IRh(CO)(P∼O)$_2$. Complex **8** (64 mg, 0.1 mmol) was treated with 0.2 mL (3.2 mmol) of methyl iodide in 5 mL of dichloromethane. The solution was stirred for approximately 1 h, and the solvent was removed under reduced pressure. The residue was dissolved in 2 mL of dichloromethane, and 30 mL of *n*-hexane was added to the solution. The yellow precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo. MS (FD, 8 kV, 35 °C): *m/e* 770 $[IRh(CO)(P{\sim}O)_2]^+$. IR (CH$_2$Cl$_2$, cm^{-1}): $\nu_{as}(C_2O)$ 1107. $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$, −30 °C): δ 27.6 (d, $^1J_{RhP}$ = 117 Hz). Anal. Calcd for $C_{31}H_{58}IO_3P_2Rh$: C, 48.32; H, 7.59; Rh, 13.35. Found: C, 48.07; H, 7.53; Rh, 13.34.

Interconversion of Complexes 3, 7, and 8. A solution of **2** (62 mg, 0.1 mmol) in 5 mL of dichloromethane was placed under 5-bar pressure of CO at −40 °C in a Schlenk tube to give **3**, which is only stable under an atmosphere of carbon monoxide at −40 °C and cannot be isolated. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡O) 2017, $\nu_{as}(C_2O)$ 1108. $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$, −30 °C): δ 48.4 (d, $^1J_{RhP}$ = 70 Hz).

Argon was bubbled through the solution of **3** at −40 °C for approximately 3 h, and the solvent was reduced to 2 mL. A 30-mL portion of *n*-hexane was added to the concentrated solution, and the crude product **7** was precipitated as a yellow solid and dried in vacuo. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡O) 2017, $\nu_{as}(C_2O)$ 1110. $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$, −30 °C): δ 31.5 (d, $^1J_{RhP}$ = 118.9 Hz).

A solution of **8** in 5 mL of dichloromethane was prepared by UV photolysis of **7** (68 mg, 0.1 mmol) at 20 °C until no **7** remained, as determined by IR spectroscopy. After the solvent was removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and 30 mL of *n*-hexane was added to the solution. The yellow precipitated mixture of **8** and the dimer $[(\mu\text{-}CO)Rh(O,P)]_2$[12] was dried in vacuo. IR (CH$_2$Cl$_2$, cm^{-1}): ν-

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[11] (a) Although high temperature and V$_2$O$_5$ (catalyst) was used for C, H analyses, the carbon values remained low. This is probably due to incomplete combustion, which may be caused by rhodium. (b) Nappier, T. E., Jr.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194.

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Table I. X-ray Diffraction Data for 4c

formula	$C_{58}H_{85}BClO_3P_2Rh\cdot CHCl_3$
mol wt	1160.7
cryst syst	monoclinic
space group	*P*2/*n*
a, Å	21.881(4)
b, Å	10.303(2)
c, Å	26.516(5)
β, deg	100.91(3)
V, Å^3	5870(2)
Z	4
d_{calcd}, g cm^{-3}	1.313
T, °C	−100
F(000), e	2448
μ(Mo Kα), mm^{-1}	0.570
2*θ* limits, deg	4–40
scan	*ω*
hkl ranges	−21 to 21, −9 to 9, −25 to 25
no. of rflns measd	21 065
no. of unique data with $I \geq 2\sigma(I)$	3242
no. of variables	583
S	0.67
R	0.044
R_w	0.043

(C≡O) 1987, $\nu_{as}(C_2O)$ 1107, 1075, $\nu(\mu\text{-CO})$ 1712. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −65 °C): δ 44.2 (d, $^1J_{RhP}$ = 111.9 Hz), 31.47 (d, $^1J_{RhP}$ = 119.1 Hz).

X-ray Structure Determination of 4c. A suitable crystal with approximate dimensions 0.2 × 0.3 × 0.3 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer with low-temperature equipment. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters and specific data collection parameters for **4c** are summarized in Table I. Intensities were collected with graphite-monochromatized Mo Kα radiation using the *ω*-scan technique with scan speed varying from 10 to 30°/min in *ω*. The structure was solved by direct methods[13] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 0.39 and −0.43 e Å^{-3}, respectively. The asymmetric unit contains one solvent molecule of $CHCl_3$. Final atomic coordinates are collected in Table II.

Results and Discussion

Treatment of the starting compound $[(\mu\text{-Cl})Rh(COE)_2]_2$ (**1**) with the PO ligand $(C_6H_{11})_2PCH_2CH_2OCH_3$ in acetone in the presence of $NaBPh_4$ results in the formation of the cationic bis(chelate) complex **2** (Scheme I). At −30 °C the $^{31}P\{^1H\}$ NMR spectrum of **2** consists of an A_2X system (Table III) caused by two equivalent phosphorus atoms in a square-planar rhodium complex. The relatively large coupling constant $^1J_{RhP}$ is in accordance with the lower trans influence of the ether oxygen atoms being trans to the phosphines.[14–16] The ^{31}P chemical shift is characteristic of a five-membered chelate ring in which an ether phosphine is involved. The relationship between ^{31}P chemical shift and ring size has recently been studied in our group.[17]

Table II. Atomic Coordinates (×10^4, Esd's in Parentheses) for 4c with Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)[a]

atom	*x*	*y*	*z*	U_{eq}
Rh(1)	2736(1)	1671(1)	213(1)	34(1)
Cl(1)	2704(1)	3989(2)	169(1)	44(1)
P(1)	3513(1)	1748(3)	917(1)	34(1)
P(2)	2571(1)	−565(2)	235(1)	35(1)
O(1)	2086(2)	2010(6)	828(2)	44(2)
O(2)	1829(2)	1585(7)	−340(2)	46(2)
O(3)	3785(3)	1088(6)	−240(2)	50(3)
C(49)	3036(4)	1762(10)	1422(3)	43(3)
C(50)	2457(4)	2567(10)	1274(3)	49(4)
C(51)	1483(4)	2611(11)	706(4)	69(5)
C(52)	1739(4)	−595(9)	−59(3)	43(4)
C(53)	1571(5)	341(10)	−499(4)	57(4)
C(54)	1529(5)	2594(10)	−671(4)	62(4)
C(55)	3285(4)	1619(10)	−305(3)	37(3)
C(56)	3071(4)	2428(9)	−795(3)	47(4)
C(57)	3578(4)	3425(10)	−844(3)	59(4)
C(58)	2962(5)	1540(11)	−1269(3)	64(4)
C(25)	4349(4)	3414(11)	1575(3)	54(4)
C(26)	4583(4)	4823(10)	1662(4)	53(4)
C(27)	4942(5)	5240(10)	1256(4)	62(5)
C(28)	4563(5)	5067(11)	727(4)	70(5)
C(29)	4309(4)	3702(9)	625(3)	47(4)
C(30)	3947(4)	3280(10)	1034(3)	38(3)
C(31)	4205(5)	22(10)	1658(3)	52(4)
C(32)	4604(5)	−1211(10)	1750(4)	61(5)
C(33)	5202(5)	−1067(10)	1549(4)	69(5)
C(34)	5072(4)	−698(10)	989(4)	55(4)
C(35)	4683(4)	536(9)	889(4)	48(4)
C(36)	4061(4)	377(9)	1084(3)	39(4)
C(37)	3639(4)	−1860(10)	34(3)	50(4)
C(38)	3901(5)	−2909(12)	−281(4)	81(5)
C(39)	3729(5)	−2700(12)	−839(4)	82(6)
C(40)	3041(5)	−2616(11)	−1007(4)	68(5)
C(41)	2763(5)	−1559(12)	−715(4)	70(5)
C(42)	2931(4)	−1712(10)	−152(3)	48(4)
C(43)	2661(4)	−2866(10)	870(3)	53(4)
C(44)	2756(5)	−3415(10)	1406(3)	61(4)
C(45)	2235(5)	−3043(12)	1678(4)	70(5)
C(46)	2150(5)	−1566(12)	1674(4)	66(5)
C(47)	2049(4)	−1055(10)	1131(3)	49(4)
C(48)	2600(4)	−1391(8)	869(3)	38(4)
B(1)	171(5)	−1542(13)	−1560(4)	51(4)
C(1)	1082(3)	−375(6)	−1927(2)	62(5)
C(2)	1506	−282	−2257	70(5)
C(3)	1470	−1144	−2668	67(5)
C(4)	1010	−2099	−2747	53(4)
C(5)	586	−2192	−2416	45(4)
C(6)	622	−1330	−2006	48(4)
C(7)	−82(3)	115(7)	−837(3)	49(4)
C(8)	−264	1325	−681	64(5)
C(9)	−379	2343	−1033	74(6)
C(10)	−312	2151	−1541	75(5)
C(11)	−129	941	−1696	68(5)
C(12)	−14	−77	−1344	47(4)
C(13)	231(2)	−2907(7)	−703(3)	56(4)
C(14)	527	−3723	−312	60(5)
C(15)	1134	−4143	−308	61(5)
C(16)	1445	−3747	−695	56(4)
C(17)	1149	−2931	−1086	44(4)
C(18)	542	−2511	−1090	49(4)
C(19)	−1032(3)	−1594(6)	−2033(2)	49(4)
C(20)	−1572	−2231	−2272	67(5)
C(21)	−1579	−3581	−2312	72(6)
C(22)	−1047	−4295	−2112	61(5)
C(23)	−507	−3659	−1873	52(4)
C(24)	−499	−2308	−1833	49(4)
Cl(2)	9182(2)	6283(4)	1945(2)	124(2)
Cl(3)	7932(2)	5351(4)	1777(1)	119(2)
Cl(4)	8628(2)	5653(5)	2805(1)	132(2)
C(59)	8658(5)	5278(12)	2175(4)	78(5)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Oxidative Addition. Oxidative addition of the acyl halides RC(O)Cl to the cationic bis(chelate) complex **2** affords the octahedral complexes **4a–e** (Scheme I). The $^{31}P\{^1H\}$ NMR spectra at −30 °C display ABX patterns (Table III), which indicate two different phosphorus nuclei.

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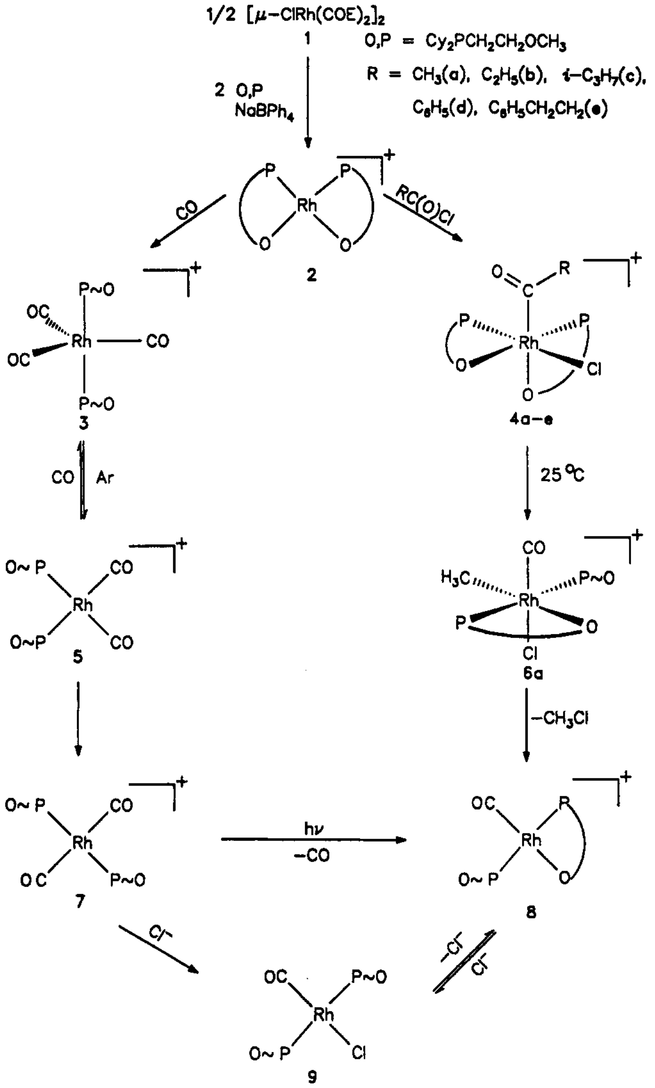
Scheme I



The coupling constants $^2J_{PP}$ of approximately 20 Hz are in agreement with two phosphorus atoms in cis positions. An analysis of the spectra of **4a–e** leads to two different $^1J_{RhP}$ coupling constants, in which the smaller value is assigned to the phosphorus trans to the ether oxygen atom. The assignment is based on the comparison of **4a** and **4′a**, which only differ by X (X = Cl, Br). In order to prove the cis position of the acyl carbon atom to both phosphorus atoms ^{13}C-labeled $CH_3{}^{13}C(O)Cl$ was used for the oxidative addition to complex **2**. The coupling constant $^2J_{PC}$ was found to be 5.5 Hz.[18]

IR spectroscopic investigations of the cationic complexes **2** and **4a–e** corroborate the ^{31}P NMR findings. In both cases $\nu_{as}(C_2O)$ is shifted to lower wavelengths (Table III). This phenomenon is diagnostic for a rhodium–oxygen contact.[19] In the IR spectra of the cationic complexes **4a–e** a >C=O band appears between 1650 and 1700 cm^{-1} (Table III). Complex **2** and to some extent also the acyl complexes **4a–e** decompose in solution and slowly in the solid state at −40 and 0 °C, respectively.

To get an insight into the mechanism of the oxidative addition of acyl halides to complex **2**, the latter was reacted

Table III. $^{31}P\{^1H\}$ NMR Data (CH_2Cl_2, −30 °C; Chemical Shifts δ in ppm, Coupling Constants *J* in Hz) and IR Data (C≡O, 〉C=O, and Antisymmetric C_2O Absorptions; cm^{-1})

	^{31}P NMR[a]				IR		
complex	δ	$^1J_{RhP}$	$^2J_{PP}$	$^2J_{PC}$	ν(C≡O)	ν(〉C=O)	$\nu_{as}(C_2O)$
2[b,c]	68.3 (d)	198.2					1067 (m)
3[d,e]	48.4 (d)	70.1			2017 (vs)		1108 (s)
4a[c,d]	48.0 (dd)	167.0	21.3			1698 (m)	1075 (m)
	43.2 (dd)	140.2	21.3				
4a′[c,d]	48.5 (ddd)	166.4	21.2	5.5		1662 (m)	1064 (m)
	43.2 (ddd)	140.0	21.2	5.5			
4b[c,d]	48.2 (dd)	167.9	21.4			1685 (m)	1073 (m)
	43.2 (dd)	141.0	21.4				
4c[b,c]	47.9 (dd)	169.2	21.7			1691 (m)	1075 (m)
	42.7 (dd)	142.0	21.7				
4d[b,c]	48.9 (dd)	166.5	19.8			1653 (m)	1075 (m)
	45.0 (dd)	137.1	19.8				
4e[b,c]	49.2 (dd)	166.9	19.8			1685 (m)	1076 (m)
	44.3 (dd)	139.5	19.8				
4′a[d,e]	49.3 (dd)	186.0	19.8			1703 (m)	1075 (m)
	44.3 (dd)	146.3	19.8				
5[d,e]	32.8 (d)	102.1			2014 (m) 1978 (s)		1110 (m)
7[b,c]	31.5 (d)	118.9			2017 (s)		1110 (m)
8[b,c]	44.2 (d)	111.9			1987 (s)		1107 (m) 1075 (m)
9[b,c]	27.6 (d)	117.1			1953 (vs)		

[a] ^{31}P NMR spectra obtained in CH_2Cl_2. [b] Isolated complexes yielded analyses for C, H, Rh (±1%). [c] KBr. [d] Unstable, not isolated. [e] IR spectra obtained in CH_2Cl_2.

with acetyl iodide, bromide, and chloride. While in the case of $CH_3C(O)I$ no significant reaction takes place, the products formed with $CH_3C(O)Br$ (**4′a**) and $CH_3C(O)Cl$ (**4a**) show ABX patterns in the $^{31}P\{^1H\}$ NMR spectra with similar chemical shifts and comparable coupling constants (Table III). Further evidence for the unstable complex **4′a** is the IR (Table III) and the mass spectrum. However, the reaction between $CH_3C(O)Br$ and **2** does not proceed quantitatively. Obviously the electrophilicity of the acyl carbon atom in $CH_3C(O)I$ is not strong enough to be attacked by the rhodium complex **2**.

It is known that BPh_4^- is able to split off a phenyl radical.[20,21] Several years ago, it was reported that the oxidative addition of $CH_3C(O)Cl$ to cationic palladium complexes containing the BPh_4^- anion proceeds via a radical mechanism.[22] To decide which of these mechanisms operates in the formation of **4a**, ^{1}H CIDNP investigations were carried out in CD_2Cl_2 at −20 °C. No polarized absorptions or emissions[23] could be observed. ESR monitoring of the reaction between complex **2** and $CH_3C(O)Cl$ points to no or only very little paramagnetic components (concentration $<10^{-7}$ M). While not conclusive, these experiments provide no support for a radical pathway. Additional evidence is obtained by applying ClO_4^- as a counterion. **4a**[ClO_4] is formed under the same reaction conditions.

To get information on how steric effects influence the oxidative addition, the behavior of the acyl chlorides RC(O)Cl (R = CH_3, C_2H_5, *i*-C_3H_7, C_6H_5, $C_6H_5CH_2CH_2$, *t*-C_4H_9) toward **2** was studied. *t*-BuC(O)Cl does not react with complex **2**, because of its steric requirement in the formation of a tetrahedral intermediate at the acyl carbon atom. The bond angles change from 120 to 109°; hence,

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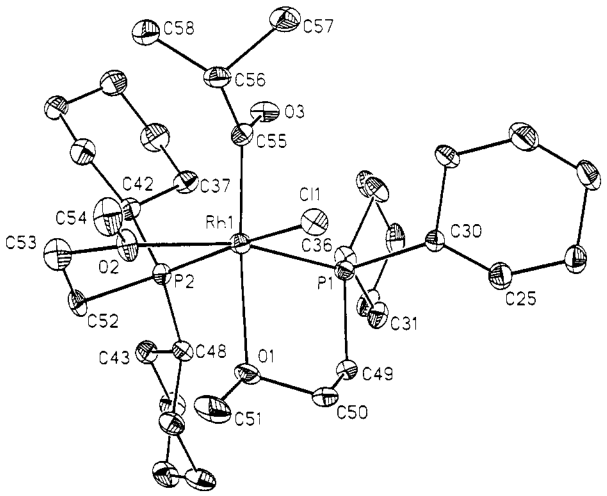

Figure 1. ORTEP plot of **4c**.

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

Bond Lengths			
Rh(1)–Cl(1)	2.392(3)	Rh(1)–P(1)	2.276(2)
Rh(1)–P(2)	2.334(3)	Rh(1)–O(1)	2.385(6)
Rh(1)–O(2)	2.236(5)	Rh(1)–C(55)	1.988(9)
O(3)–C(55)	1.205(12)	C(55)–C(56)	1.541(12)
O(1)–C(51)	1.436(10)	O(1)–C(50)	1.424(10)
O(2)–C(54)	1.437(12)	O(2)–C(53)	1.430(12)
Bond Angles			
P(1)–Rh(1)–P(2)	96.3(1)	P(1)–Rh(1)–O(1)	83.3(1)
P(2)–Rh(1)–O(1)	90.7(2)	Cl(1)–Rh(1)–P(1)	90.9(1)
Cl(1)–Rh(1)–C(55)	90.6(3)	Cl(1)–Rh(1)–O(1)	82.6(2)
C(50)–O(1)–C(51)	111.6(7)	C(53)–O(2)–C(54)	111.1(6)
Cl(1)–Rh(1)–C(55)	90.6(3)	Rh(1)–C(55)–O(3)	124.3(6)

big R groups do not foster the reaction. On the basis of all investigations mentioned in this section, the reaction should proceed as follows: after the nucleophilic attack of complex **2** to the acyl carbon atom, the chloride is split from the corresponding acyl carbon atom, resulting in the formation of the unstable intermediate. The chloride then attacks the intermediate, yielding the final products **4a–e**.[24]

In a previous paper[25] it was found that there is a trend toward greater ease of alkyl migration with increasing chain length and branched alkyl groups, and steric crowding in the transition state may increase the activation energy. Larger substituents R shield the acyl group from being subjected to reverse alkyl migration, and six-coordinate complexes of the type [Rh(P⌒O)(P∼O)R(CO)Cl]BPh$_4$] (**6**) would undoubtedly be more crowded than complexes of the type [Rh(P⌒O)$_2$C(O)RCl][BPh$_4$] (**4**).[26] Taking these factors into account, it is not surprising that the acyl complex with an isopropyl group shows an unusual stability. **4c** can be isolated and recrystallized from a mixture of chloroform and *n*-hexane. The structure of complex **4c** has been determined by X-ray diffraction.

Description of the Crystal Structure of 4c. The crystal structure of **4c** is depicted in Figure 1. Table IV contains selected bond distances and angles. The coordination octahedron is distorted due to the steric demand of the cis-oriented PCy$_2$ groups and the presence of two five-membered chelate rings with different conformations. The angles P(1)–Rh(1)–O(1) and P(2)–Rh(1)–O(2) are below 90°, while that of P(1)–Rh(1)–P(2) is above. The five-membered ring with the atomic sequence Rh(1)–P(1)–C(49)–C(50)–O(1) forms an envelope. That with the sequence Rh(1)–P(2)–C(52)–C(53)–O(2) has a twist conformation, which agrees with torsional angles 8.1° (O(1)–Rh(1)–P(1)–C(49)) and –15.7° (O(2)–Rh(1)–P(2)–C(52)), respectively. The Rh(1)–P(2) and Rh(1)–O(1) bond lengths are significantly longer than those of Rh(1)–P(1) and Rh(1)–O(2), which can be explained in terms of the lower trans influence of the ether oxygen and the phosphorus atom, compared to the phosphorus and acyl carbon atom, respectively. The Rh(1)–C(55), C(55)–O(3), and Rh(1)–Cl(1) bond lengths agree with those reported in the literature for similar compounds.[27,28]

Evidence of the Reverse Methyl Migration. Because of reverse methyl migration, a second band appears at approximately 2065 cm^{-1} in the IR spectra of **4a**. This band is attributed to the vibration of the terminal CO group of **6a**. The absorption of high frequency indicates that the CO group is trans to a ligand with weak trans influence, chloride or the ether oxygen atom.[29] In the case of the ^{13}C-labeled complexes **4a′** and **6a′** the same shift of both acyl and terminal CO absorptions demonstrates that the terminal CO stems from the acyl group (Table III). When **4a** is warmed from –20 to 20 °C in CD$_2$Cl$_2$, a broad doublet appears at 46.19 ppm ($^1J_{RhP}$ = 132.2 Hz) in the ^{31}P{^{1}H} NMR spectrum. This agrees with the formation of complex **6a** through reverse methyl migration (Scheme I). The doublet results from the fast exchange of the two different phosphorus nuclei, which is comparable with that of complex **8** having both η^2- and η^1-ether–phosphine functions in one molecule. The magnitude of $^1J_{RhP}$ is consistent with two phosphorus atoms in trans positions.[30] In the ^{13}C{^{1}H} NMR spectrum of the ^{13}C-labeled complex [(P∼O)(P⌒O)Rh^{13}CH$_3$(CO)Cl][BPh$_4$] (**6a″**) a doublet appears at –4.0 ppm with $^1J_{RhC}$ = 19.3 Hz (100.62 MHz, CD$_2$Cl$_2$, 303 K). This chemical shift and this coupling constant of **6a″** are comparable with those of other rhodium methyl complexes.[31] All spectroscopic evidence supports the occurrence of a reverse methyl migration to **6a**, which is an intermediate in the reductive elimination of CH$_3$Cl from **4a**.

Reductive Elimination. Treatment of **4a** with a mixture of THF and water and carbon monoxide yields complex **9** as the exclusive final product. During the course of the reaction only a small amount of CH$_3$CO$_2$H was detected by GC. These results suggest that almost no reductive elimination of CH$_3$C(O)Cl from **4a** takes place. Therefore, this process was monitored in dichloromethane at –20 °C by ^{31}P{^{1}H} NMR spectroscopy and GC–MS. While the temperature was raised from –20 to 0 °C, a broad doublet appeared at 46.19 ppm ($^1J_{RhP}$ = 132.2 Hz), which is in agreement with complex **6a** formed from a reverse methyl migration (Scheme I). At the expense of the above-mentioned doublet a new one appeared after 30

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min at 45.2 ppm ($^1J_{RhP}$ = 113.6 Hz), which is assigned to complex 8. Subsequently, another doublet at 27.8 ppm ($^1J_{RhP}$ = 118.7 Hz) was observed, owing to the fact that complex 9 was formed (Scheme I). The reaction solution was then analyzed by GC–MS, and CH_3Cl, benzene, and biphenyl were detected. Due to the reductive elimination **4a** differs from the product 9 by loss of the methyl group. The treatment of complex 8 with CH_3I affords IRh(CO)(P~O)$_2$, biphenyl, and toluene. Both organic products were detected by GC–MS and are assumed to be formed by decomposition of the counterion (BPh_4^-)[20,21] and interaction of the methyl group with the counterion, respectively. These results establish the formation of complex 9 and give an explanation of the fate of the methyl group. The process can be summarized in three steps: (i) **4a** is subject to a reverse methyl migration, yielding **6a**; (ii) the reductive elimination of methyl chloride from complex **6a** results in the formation of complex 8; (iii) the formation of complex 9 as the final product is observed in the $^{31}P\{^1H\}$ NMR spectrum.

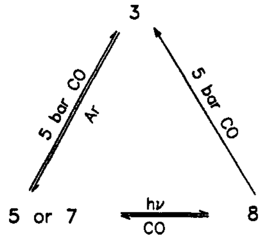
Reverse alkyl migration takes place only when a free coordination site is available.[32] As already mentioned, rhodium(III) is more oxophilic than rhodium(I); hence, bis($O\frown P$-chelate) complexes are usually more preferred.[6,33] The more basic PO ligand $Cy_2PCH_2CH_2OCH_3$ makes rhodium(III) less oxophilic and therefore *weakens* the rhodium–oxygen bond. A free coordination site is obtained by dissociating an oxygen donor from rhodium without separating from the complex fragment, which is called the intramolecular solvent function of ether–phosphine ligands. Our investigations and results of reductive elimination are in agreement with the occurrence of a reverse methyl migration from **4a**.

Carbonylation of Complex 2. To investigate the reactivity of the both Rh–O bonds, the bis(chelate) complex 2 was allowed to react with 5-bar pressure of carbon monoxide in dichloromethane at −40 °C. Both Rh–O bonds were immediately cleaved, forming the cationic tricarbonyl complex 3, which was characterized by IR and $^{31}P\{^1H\}$ NMR spectroscopy (Table III).[33] 3 is only stable at −40 °C under an atmosphere of carbon monoxide.

When argon is bubbled through a dichloromethane solution of 3 at −40 °C, the *cis*-dicarbonyl species 5 is formed instead of the expected 8.[6,33] Complexes of this type are stabilized either by η^2-bonded ligands[34,35] or strongly basic η^1(P)-coordinated phosphines.[36,37] The higher electron density at rhodium is the reason for a stronger Rh–CO π bond and the formation of dicarbonyl species.

As expected, complex 5 shows two strong CO absorptions in the IR spectrum. An extremely small coupling constant $^1J_{RhP}$ results from the high trans influence of the CO groups (Table III). The *cis*-dicarbonylrhodium(I) complex 5 is a kinetically favored product and is easily transformed into the thermodynamically more stable *trans*-dicarbonylrhodium(I) complex 7. In the IR spectrum of 7 only one CO absorption (ν_{as}(CO) = 2017 cm^{-1}) was observed. The $^{13}C\{^1H\}$ NMR spectrum of complex 7 consists of an A_2M_2X system, showing a doublet of triplets, thus indicating cis positions of both carbonyl groups to the phosphorus atoms. Only one doublet appears in the $^{31}P\{^1H\}$ NMR spectrum of 5 or 7, the position of which is characteristic of η^1(P)-bonded ether–phosphines[6] (Table III).

Scheme II



UV irradiation of complex 7 in CH_2Cl_2 solution generates the monocarbonyl species 8, which could be identified only spectroscopically (IR, MS, and $^{31}P\{^1H\}$ NMR[6]) (Table III), because there exists an equilibrium between monomeric complex 8 and the dimer [(μ-CO)Rh(O,P)]$_2$. This equilibrium was thoroughly studied, and the results will be published in a forthcoming paper.[12]

Each of the complexes 5, 7, and 8 shows an absorption at 1107 cm^{-1} for ν_{as}(C_2O), which indicates a noncoordinated ether oxygen atom. In the case of 8, two bands are observed at 1107 and 1075 cm^{-1}, revealing the occurrence of both η^2- and η^1-ether–phosphine functions.

Interconversion of Complexes 3, 7, and 8. When argon is bubbled through a CH_2Cl_2 solution of 3, complexes 5 and 7 are formed. UV irradiation of 5 or 7 yields the monocarbonyl complex 8. 5, 7, and 8 react with 5-bar pressure of CO to give the tricarbonylrhodium(I) complex 3. The process was confirmed by IR and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme II).

Conclusion

The basicity of ether–phosphine ligands plays a very important role in both reversible alkyl migration and the chemistry of bis(chelate) complex 2 with carbon monoxide. The course of the alkyl migration can be controlled by ether–phosphines of different basicity. With ligands of lower basicity "CO insertion" is preferred. With those of stronger basicity reverse alkyl migration takes place. Ether–phosphine ligands function as intramolecular solvents, and as a result of the "opening and closing mechanism" empty coordination sites are made available and promote reverse alkyl migration. With ether–phosphines of stronger basicity dicarbonylrhodium(I) complexes are favored compared to monocarbonyl species.

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Supplementary Material Available: Tables of crystal data and data collection and refinement details and interatomic distances and angles for **4c** (5 pages). Ordering information is given on any current masthead page.

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