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Synthesis, Dynamic Behavior, and Catalytic Activity of the Ether–Phosphine Complex Rh($P^\frown O$)($P\sim O$)Cl and Its Reactivity toward Hydrogen, Oxygen, Methyl Iodide, and Acetyl Chloride

Ekkehard Lindner,* Qinyan Wang, Hermann August Mayer, Armin Bader, Hartwig Kühbauch, and Peter Wegner

Institut für Anorganische Chemie der Universität, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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The complex ClRh($P\sim O$)($P^\frown O$) (1; $P^\frown O$ = η^2(O,P)-chelated $Cy_2PCH_2CH_2OCH_3$ ligand; $P\sim O$ = η^1(P) coordinated) exhibits fluxional behavior on the ^{31}P NMR time scale. Line-shape analysis of variable-temperature $^{31}P\{^1H\}$ NMR spectra of 1 yields values of $\Delta H^\ddagger = 43.0 \pm 3.4$ kJ mol^{-1} and $\Delta S^\ddagger = -42 \pm 11.8$ J mol^{-1} K^{-1}, indicating an associative mechanism of the dynamic process involving a five-coordinate species. Hydrogenation of 1-hexene to *n*-hexane over complex 1 as precatalyst proceeds with 100% selectivity and excellent activity (turnover number 7920 h^{-1}) under mild conditions (300 K, 40 bar of H_2). Oxidative addition of H_2 and O_2 results in the formation of the unstable dihydridorhodium(III) complex $ClRhH_2(P\sim O)_2$ (2) and the relatively stable (dioxygen)rhodium(III) complex $ClRhO_2(P\sim O)(P^\frown O)$ (3), respectively. The reaction of methyl iodide and acetyl chloride with complex 1 affords the products of the oxidative addition in *trans* fashion (CH_3(Cl)(I)Rh($P\sim O$)($P^\frown O$) (**5a**), $CH_3C(O)Cl_2Rh(P\sim O)(P^\frown O)$ (**6a**)) and *cis* fashion ($CH_3(Cl)(I)Rh(P\sim O)_2$ (**5b**), $CH_3(I)(Cl)Rh(P\sim O)_2$ (**5c**), $CH_3C(O)Cl_2Rh(P\sim O)_2$ (**6b**)). The use of labeled $^{13}CH_3I$ and $CH_3{}^{13}C(O)Cl$ supports the structural characterization of all isomers by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. When it is warmed in $CDCl_3$, **5a′** is irreversibly converted into **5b′** and **5c′** (**5a′**, **5b′**, and **5c′** = $^{13}CH_3$-labeled isomers of complex **5**). First-order kinetics in **5a′** with a rate constant of 7.67×10^{-5} s^{-1} at 287 K is established. The carbonylation of **5b** (**5b′**) gives a mixture of $IRhCO(P\sim O)_2$ (**8**) and $CH_3C(O)Rh(I)(Cl)(P\sim O)_2$ (**9**; **9′** = $CH_3{}^{13}C$-(O)-labeled analogue of **9**) *via* the unstable intermediate **7**. The progress of the reaction is monitored, and the compounds **8**, **9** (**9′**), and $^{13}CH_3Cl$ are identified by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy.

Introduction

The discovery by Wilkinson that $RhCl(PPh_3)_3$ is an efficient homogeneous hydrogenation catalyst has spurred mechanistic studies which have led to an improved understanding of its functioning at a molecular level.[1,2] Although there is still a great deal of speculation, the external solvent complex $RhCl(PPh_3)_2(S)$ (S = solvent) has been postulated to be a reactive species in the catalytic cycle and cannot be isolated.[3,4] The introduction of ether–phosphine species instead of "classical" phosphines, however, has made it possible to prepare intramolecular solvent complexes which, due to O,P chelation, are much more stable than simple solvent adducts and can therefore be isolated and examined in detail.[5] A range of (ether–phosphine)ruthenium and -palladium complexes exhibit fluxional behavior at rates slow enough to be studied by ^{31}P NMR spectroscopy. Valuable thermodynamic data on the relative stability of metal–oxygen bonds could be obtained in this way.[6,7] With a view to investigating the properties and reactivity of solvent complexes derived from the Wilkinson catalyst, the isolable compound RhCl($P^\frown O$)-($P\sim O$) ($P^\frown O$ = η^2(O,P)-chelated $Cy_2PCH_2CH_2OCH_3$ ligand; $P\sim O$ = η^1(P) coordination of the same ligand) was prepared as the analogue of unstable $RhCl(PPh_3)_2(S)$. This work also presents the reactions of the title complex with small molecules, *viz.* hydrogen, oxygen, methyl iodide, and acetyl chloride.

Experimental Section

General Procedures. All operations were performed under dry, oxygen-free argon applying the usual Schlenk techniques. Solvents were purified by standard methods and stored under argon. Instrumentation: mass spectra, Finnigan MAT 711 A (modified by AMD); IR, Bruker FT-IR spectrometer, Model IFS 48; ^1H and $^{13}C\{^1H\}$ NMR, Bruker AC 80 and Bruker AC 250 at 80.13, 20.15 and 250.13, 62.90 MHz, respectively; $^{31}P\{^1H\}$ NMR, Bruker WP 80 and AC 80 at 32.39 and 32.44 MHz, respectively, external standard at low temperatures (0 to −80 °C) 1% H_3PO_4 in acetone-d_6 and at high temperatures (0–50 °C) 1% H_3PO_4 in D_2O. Elemental analyses were carried out on a Carlo Erba Model 1106 elemental analyzer and on a Perkin-Elmer Model 4000 atomic absorption spectrometer. The starting compounds $[(\mu\text{-}Cl)Rh(COE)_2]_2$[8] (COE = cyclooctene) and dicyclohexyl(methoxyethyl)phosphine $(C_6H_{11})_2PCH_2CH_2OCH_3$ (O,P)[9] were prepared according to published procedures.

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^{31}P DNMR. ^{31}P DNMR experiments were performed on a Bruker AC 80 using a 10-mm-o.d. NMR sample tube. The temperature was measured with a temperature control unit (Bruker VT 100 instrument) and an external thermocouple (PT 100). The NMR probe temperature was calibrated by the method of van Geet[10] and is considered accurate to ±1 K (about 20 min was required for the temperature equilibration of the NMR sample). All exchange-broadened NMR spectra were simulated by applying a modified version of DNMR5[11] available from the Quantum Chemistry Program Exchange (QCMP No. 365). From the resulting rate constants the pertinent thermodynamic parameters were calculated with the nonlinear least-squares program ACTPAR.[12] Reported errors are with standard deviation.

Hydrogenations. Air was removed from a 100-mL stainless steel autoclave containing the catalyst and 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). Hydrogenation of 1-hexene to *n*-hexane over complex 1 as precatalyst proceeds with 100% selectivity and excellent activity (turnover number 7920 h^{-1}) under mild conditions (for example, under the conditions of 300 K and 40 bar of H_2, molar ratio 1-hexene (neat):Rh = 10^3 and initial amount of 1 0.1 mmol).

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*;*O′*,*P′*]-rhodium(I) (1). A 105-mg (0.4-mmol) amount of the ligand $(C_6H_{11})_2PCH_2CH_2OCH_3$ (O,P) was added to a solution of $[(\mu\text{-}Cl)Rh(COE)_2]_2$ (72 mg, 0.1 mmol) in 10 mL of *n*-hexane, and the solution was stirred for 10 min at 0 °C. Red crystals were obtained by cooling the solution slowly. The precipitate was collected and dried in vacuo. The product is very air-sensitive and decomposes slowly, even at −40 °C: yield 20.3 mg (31.2%); mp 82 °C dec; MS (FD, 8 kV, 35 °C) *m/e* 650 $[Rh(P^\frown O)(P{\sim}O)Cl]^+$. Anal. Calcd for $C_{30}H_{58}ClO_2P_2Rh$: C, 55.34; H, 8.98; Rh, 15.80. Found: C, 54.79; H, 9.05; Rh, 16.60.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]dihydridorhodium(III) (2). A solution of 1 (65 mg, 0.1 mmol) in 5 mL of acetone (or dichloromethane) was stirred at −40 °C under an atmosphere of hydrogen (1 bar) until a pale yellow solution was obtained. The reaction takes approximately 30 min. **2** is only stable under an atmosphere of hydrogen and cannot be isolated: ^{1}H NMR (250.13 MHz, acetone-d_6, 303 K) δ −22.57 (dt, $^1J_{RhH}$ = 27.0, $^2J_{PH}$ = 15.8 Hz, RhH_2); MS (FD, 8 kV, 35 °C) *m/e* 650 $[Rh(P^\frown O)(P{\sim}O)Cl]^+$; IR ($CH_2Cl_2$, cm^{-1}) 2145 (m, RhH_2).

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*;*O′*,*P′*]-(dioxygen)rhodium(III) (3). A solution of 1 (65 mg, 0.1 mmol) was treated with oxygen (1 bar) in 10 mL of *n*-hexane at −40 °C until a dark brown solution was obtained. The reaction takes approximately 30 min. The pale yellow solid was precipitated by cooling the solution. The precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo to yield 56.0 mg (82.0%) of the crude product: mp 78 °C dec; MS (FAB, 35 °C) *m/e* 683 $[Rh(P^\frown O)(P{\sim}O)ClO_2]^+$. Anal. Calcd for $C_{30}H_{58}ClO_4P_2Rh$: C, 52.75; H, 8.56; Rh, 15.06. Found: C, 52.73; H, 8.67; Rh, 14.98.

General Procedure for Complexes 5 (5′) (Mixture of 5a (5a′) and 5b (5b′)). A 0.1-mL (1.6-mmol) amount of CH_3I ($^{13}CH_3I$) was added to a solution of 1 (65 mg, 0.1 mmol) in 5 mL of *n*-hexane at 0 °C. A pale yellow solid precipitated instantaneously. The precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo. In the $^{31}P\{^1H\}$ NMR spectrum of the product in dichloromethane both **5a** (**5a′**) and **5b** (**5b′**) were observed (Table II).

Mixture of chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*;*O′*,*P′*]iodomethylrhodium(III) (5a) and chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]iodomethylrhodium(III) (5b): yield 79.0 mg (100%); mp 76 °C dec; MS (FD, 8 kV, 35 °C) *m/e* 792 $[Rh(P^\frown O)(P{\sim}O)ClCH_3I]^+$. Anal. Calcd for $C_{31}H_{61}ClIO_2P_2Rh$: C, 46.95; H, 7.94; Rh, 12.98. Found: C, 47.05; H, 7.94; Rh, 12.90.

Mixture of chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*;*O′*,*P′*]iodo(methyl-^{13}*C*)rhodium(III) (5a′) and chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]iodo(methyl-^{13}*C*)rhodium(III) (5b′): yield 79.0 mg (100%); mp 76 °C dec; $^{13}C\{^1H\}$ NMR (20.15 MHz, CD_2Cl_2, 243 K) δ −8.38 (ddd, $^1J_{RhC}$ = 23.8, $^2J_{P^1C}$ = 6.7, $^2J_{P^2C}$ = 8.1 Hz, $^{13}CH_3Rh$ for **5a′**); MS (FD, 8 kV, 35 °C) *m/e* 793 $[Rh(P^\frown O)(P{\sim}O)Cl^{13}CH_3I]^+$. Anal. Calcd for $^{13}CC_{30}H_{61}ClIO_2P_2Rh$: C, 47.02; H, 7.74; Rh, 12.96. Found: C, 46.02; H, 7.72; Rh, 12.93.

General Procedure for Complexes 5b (5b′). A 0.1-mL (1.6-mmol) amount of methyl iodide ($^{13}CH_3I$) was added to a solution of 1 (65 mg, 0.1 mmol) in 5 mL of toluene (or benzene-d_6) at 0 °C. The solution changed instantaneously from orange to dark red. The solvent was removed under reduced pressure. After the residue was redissolved in 2 mL of dichloromethane, 15 mL of *n*-hexane was added. Crude **5b** (**5b′**) was obtained as a dark yellow solid and dried in vacuo.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]-iodomethylrhodium(III) (5b): yield 62 mg (78.2%); mp 82 °C dec; MS (FD, 8 kV, 35 °C) *m/e* 792 $[Rh(P{\sim}O)_2ClCH_3I]^+$. Anal. Calcd for $C_{31}H_{61}ClIO_2P_2Rh$: C, 46.95; H, 7.75; Rh, 12.98. Found: C, 46.34; H, 7.70; Rh, 12.57.

Chlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]iodo-(methyl-^{13}*C*)rhodium(III) (5b′): yield 65 mg (82.0%); mp 83 °C dec; $^{13}C\{^1H\}$ NMR (20.15 MHz, C_6D_6, 287 K) δ −5.12 (dt, $^1J_{RhC}$ = 24.4, $^2J_{PC}$ = 9.1 Hz, $^{13}CH_3Rh$); MS (FD, 8 kV, 35 °C) *m/e* 793 $[Rh(P{\sim}O)_2Cl^{13}CH_3I]^+$. Anal. Calcd for $^{13}CC_{30}H_{61}ClIO_2P_2Rh$: C, 47.02; H, 7.74; Rh, 12.96. Found: C, 46.54; H, 7.40; Rh, 12.48.

Mixture of Acetyldichlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*;*O′*,*P′*]rhodium(III) (6a) and Acetyldichlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(III) (6b). A 0.25-mL (3.2-mmol) amount of $CH_3C(O)Cl$ was added to a solution of 1 (65 mg, 0.1 mmol) in 5 mL of *n*-hexane at 0 °C. The yellow solid precipitated instantaneously. The precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo. In the $^{31}P\{^1H\}$ NMR spectrum of the product in dichloromethane **6a** and **6b** were observed (Table II): yield 71.0 mg (97.4%); mp 72 °C dec; MS (FAB, 55 °C) *m/e* 693 $[Rh(P^\frown O)(P{\sim}O)ClCH_3C(O)]^+$. Anal. Calcd for $C_{32}H_{61}Cl_2O_3P_2Rh$: C, 52.68; H, 8.43; Rh, 14.10. Found: C, 51.45; H, 8.76; Rh, 14.00.

General Procedure for Complexes 6b (6b′). A 0.05-mL (0.6-mmol) amount of $CH_3C(O)Cl$ ($CH_3{}^{13}C(O)Cl$) was added to a solution of 1 (65 mg, 0.1 mmol) in 5 mL of *n*-hexane at 0 °C. The pale yellow solid precipitated instantaneously. The precipitate was collected, washed three times with 2 mL of *n*-hexane, and dried in vacuo.

Acetyldichlorobis[dicyclohexyl(methoxyethyl)phosphine-*P*]rhodium(III) (6b): yield 71.0 mg (97.4%); mp 70 °C dec; MS (FAB, 55 °C) *m/e* 693 $[Rh(P{\sim}O)_2ClCH_3C(O)]^+$. Anal. Calcd for $C_{32}H_{61}ClO_3P_2Rh$: C, 52.68; H, 8.43; Rh, 14.10. Found: C, 51.95; H, 8.66; Rh, 14.32.

(Acetyl-*1*-^{13}*C*)dichlorobis[dicyclohexyl(methoxyethyl)-phosphine-*P*]rhodium(III) (6b′): yield 71.0 mg (97.3%); mp 74 °C dec; $^{13}C\{^1H\}$ NMR (20.15 MHz, CD_2Cl_2, 243 K) δ 219.13 (dt, $^1J_{RhC}$ = 16.8, $^2J_{PC}$ = 6.0 Hz, $CH_3{}^{13}C(O)Rh$); MS (FAB, 55 °C) *m/e* 694 $[Rh(P{\sim}O)_2ClCH_3{}^{13}C(O)]^+$. Anal. Calcd for $^{13}CC_{31}H_{61}Cl_2O_3P_2Rh$: C, 52.75; H, 8.42; Rh, 14.09. Found: C, 51.81; H, 8.54; Rh, 13.96.

Reaction of 5b (5b′) with CO. A solution of **5b** (**5b′**) (79 mg, 0.1 mmol) in dichloromethane (2 mL) was treated with carbon monoxide (1 bar) at −30 °C for 10 min. The progress of the reaction was monitored by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. Two additional doublets appeared in the $^{31}P\{^1H\}$ NMR spectrum, which are assigned to 8 (IR (CH_2Cl_2, cm^{-1}) $\nu(C{\equiv}O)$ 1952; $^{31}P\{^1H\}$

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NMR (32.44 MHz, CH_2Cl_2, 243 K) δ 23.8 (d, $^1J_{RhP}$ = 117.4 Hz)) and 9 (IR (CH_2Cl_2, cm^{-1}) ν(>C=O) 1712; $^{31}P\{^1H\}$ NMR (32.44 MHz, CH_2Cl_2, 243 K) δ 13.5 (d, $^1J_{RhP}$ = 101.6 Hz)). Accordingly, complex 9′ and $^{13}CH_3Cl$ were detected by $^{13}C\{^1H\}$ NMR spectroscopy (9 (20.15 MHz, CD_2Cl_2, 243 K) δ 41.1 ($^{13}CH_3C(O)$); $^{13}CH_3Cl$ (20.15 MHz, CD_2Cl_2, 243 K) δ 22.43).

Kinetic Studies of the Conversion of 5a′ to 5b′ and 5c′. A kinetic study of the conversion of 5a′ to 5b′ and 5c′ was carried out in a $CDCl_3$ solution at 287 K. Further evidence for 5c′: $^{13}C\{^1H\}$ NMR (20.15 MHz, C_6D_6, 287 K) δ −6.80 (dt, $^1J_{RhC}$ = 23.6, $^2J_{PC}$ = 8.8 Hz, $^{13}CH_3Rh$). The temperature was measured using an external thermocouple (PT 100) and is considered accurate to ±1 K. The initial concentration of 5a′ was 0.1 mmol in 0.5 mL of $CDCl_3$. The reaction was followed by ^{31}P NMR, with spectra being recorded on a Bruker AC 80 spectrometer. Chemical shifts (in δ) were measured with respect to the external reference of 1% H_3PO_4 in acetone-d_6. The reaction was followed for at least 3 half-lives, and the change in concentration of 5a′ (as determined from the area of the resonances) was measured as a function of time. Spectral data were acquired over a period of 8 min at intervals of 5 min, starting immediately after dissolving the reactant 5a′.

Results and Discussion

Treatment of the starting compound $[(\mu\text{-}Cl)Rh(COE)_2]_2$ with the O,P ligand $(C_6H_{11})_2PCH_2CH_2OCH_3$ in acetone results in the formation of the neutral mono(chelate) complex 1. The $^{31}P\{^1H\}$ NMR and IR data are in agreement with those of a similar known complex.[13]

Dynamic Behavior. The fluxional behavior of complex 1 is demonstrated by variable-temperature $^{31}P\{^1H\}$ NMR spectra. The observed dynamic phenomena are reversible. At low temperatures (below 235 K in acetone) the spectrum displays a well-resolved ABX pattern. As the temperature is raised, the two phosphorus doublet–doublet resonances first become broad and then slowly coalesce; finally, at 325 K, a typical A_2X spectrum is observed. This averaging of the magnetic environments on the ^{31}P NMR time scale at this temperature indicates a rapid mutual exchange of two unequal ether moieties in complex 1. By application of a modified version of DNMR5,[11] $^{31}P\{^1H\}$ NMR spectra were simulated and iteratively fitted to the experimental spectra in order to evaluate the rate constants for the exchange process at various temperatures. Both simulated and experimental spectra are depicted in Figure 1. The analysis of the kinetic data with the Eyring equation and the nonlinear least-squares program ACTPAR[12] affords the thermodynamic parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta G^\ddagger{}_c$, and $\Delta G^\ddagger{}_{298}$ (see Table I). $\Delta G^\ddagger$ is regarded as the difference between the energies of the ground and transition states, and $\Delta H^\ddagger$ is a measure of the metal–oxygen bond strength. The entropy of the exchange process shows a large negative value, which reveals an intramolecular exchange[14,15] and further indicates that the transition state is more ordered than the ground state. On the basis of calculated thermodynamic parameters an associative mechanism involving a five-coordinate species is proposed (see Scheme I).

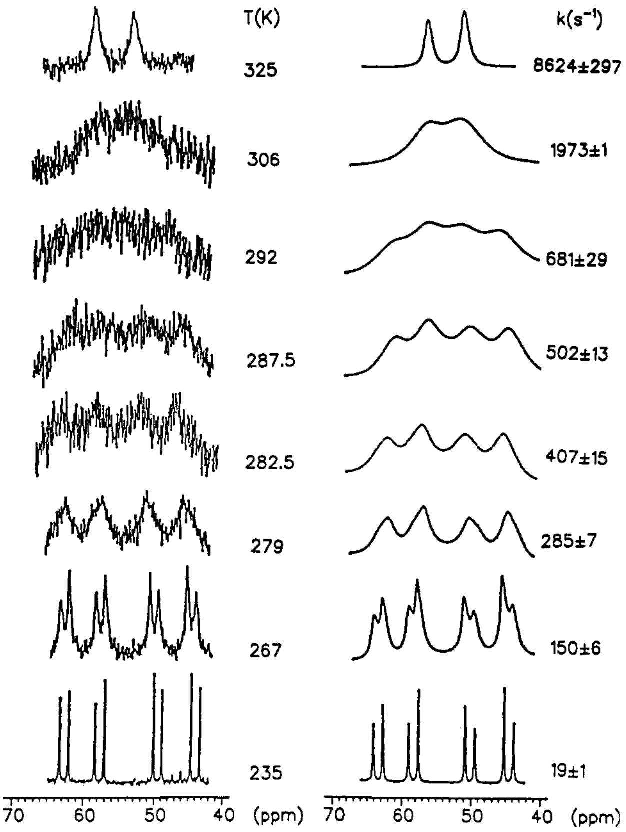


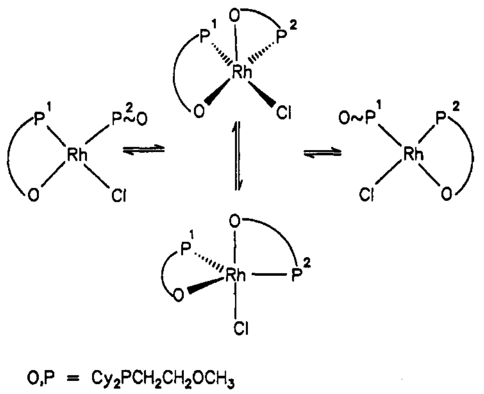
Figure 1. Experimental (left) and simulated (right) variable-temperature $^{31}P\{^1H\}$ NMR spectra and rate constants *k*, for the mutual exchange of two different ether moieties of complex 1.

Table I. Coalescence Temperature and Eyring Activation Parameters for the Fluxional Process in 1

complex	T_c/K	$\Delta H^{\ddagger\,a}$/kJ mol^{-1}	$\Delta S^{\ddagger\,a}$/J mol^{-1} K^{-1}	$\Delta G^{\ddagger\,b}$/kJ mol^{-1}	$\Delta G^{\ddagger\,c}$/kJ mol^{-1}
1	292	43.0 ± 3.4	−42 ± 11.8	55.1 ± 4.8	55.3 ± 4.9

[a] Calculated at coalescence temperature (T_c) using a modified version of DNMR5 and ACTPAR. [b] Calculated at T_c using the required law of propagation of errors. [c] Calculated at 298 K using the required law of propagation of errors.

Scheme I



O,P = $Cy_2PCH_2CH_2OCH_3$

Hydrogenation. Complex 1 is closely related to the well-known Wilkinson catalyst $RhCl(PPh_3)_3$ and should therefore be active in the hydrogenation of olefins.[1] Preliminary experiments have indeed shown that neat 1-hexene is effectively hydrogenated to *n*-hexane over 1 at moderate temperatures and pressures (see Experimental Section).

Oxidative Addition. Under smooth conditions, 1 oxidatively adds molecular hydrogen in a *cis* fashion to give the dihydridorhodium(III) complex 2 (see Scheme

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Scheme II

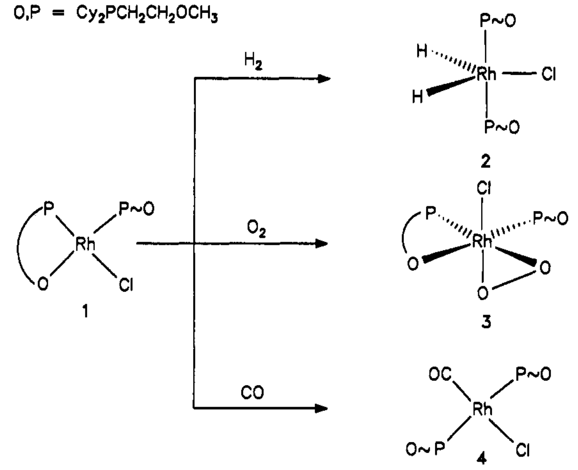

Table II. $^{31}P\{^1H\}$ **NMR Data (243 K; Chemical Shifts** δ **in ppm, Coupling Constants** J **in Hz) and IR Data (**$C{\equiv}O$**,** $>C{=}O$**, and Antisymmetric** C_2O **Absorptions; cm**$^{-1}$**)**

	^{31}P NMR				IR		
complex	δ	$^1J_{RhP}$	$^2J_{PP}$	$^2J_{PC}$	ν-($C{\equiv}O$)	ν-($>C{=}O$)	ν_{as}-(C_2O)
1[a,b]	61.0 (dd)	187.5	47.3				1105 (m)
	47.0 (dd)	208.8	47.3				1076 (m)
2[a,c]	44.7 (d)	112.8					1108 (m)
3[a,b]	44.5 (dd)	143.3	22.9				1105 (sh)
	38.6 (dd)	144.8	22.9				
5a[a,b]	50.9 (dd)	151.4	26.9				1101 (m)
	41.8 (dd)	130.0	26.9				1072 (m)
5b[b,d]	8.8 (d)	97.6					1101 (m)
5c[b,d]	5.8 (d)	90.8					1101 (m)
5a′[b,e]	46.7 (ddd)	151.8	26.4	8.1			1105 (m)
	36.8 (ddd)	130.6	26.4	6.7			1078 (m)
5b′[b,f]	3.4 (d)	98.2		9.1			1106 (m)
5c′[b,f]	0.9 (d)	90.8		8.8			1106 (m)
6a[a,b]	61.4 (dd)	126.3	24.0			1657 (m)	1107 (m)
	54.7 (dd)	144.7	24.0				1075 (m)
6b[a,b]	25.1 (d)	145.6				1715 (m)	1104 (m)
6b′[b,e]	21.2 (d)	145.7		6.0		1696 (m)	1106 (m)
7[c]					2068 (m)		
9[a,c]	15.5 (d)	101.6				1701 (m)	1106 (m)

[a] ^{31}P NMR spectra obtained in CH_2Cl_2. [b] Isolated complexes yielded correct analyses for C, H, and Rh (±0.5%); IR spectra were obtained in KBr. [c] Unstable, not isolated; IR spectra were obtained in CH_2Cl_2. [d] ^{31}P NMR spectra obtained in toluene. [e] ^{31}P NMR spectra obtained in CD_2Cl_2. [f] ^{31}P NMR spectra obtained in C_6D_6 at 283 K.

II).[13,16–19] This compound is only stable at low temperatures (below −40 °C) under an atmosphere of hydrogen and could therefore not be isolated in pure form. The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of an A_2X pattern which reveals two equivalent phosphorus atoms (see Table II). Accordingly, the analysis of the A_2M_2X type ^{1}H NMR spectrum yields a $^2J_{PH}$ coupling constant of 15.8 Hz, indicating that the hydrido ligands are *cis* to the phosphines. The RhH_2 band (2145 cm^{-1}) in the IR spectrum provides further evidence for the existence of complex **2**.

A solution of **1** in *n*-hexane readily takes up oxygen, whereupon the yellow dioxygen complex **3** is generated. The molecular geometry of **3** depicted in Scheme II was put forward on the basis of $^{31}P\{^1H\}$ NMR data, which are comparable to those of the known complex *cis*-$[Rh(P\frown O)_2O_2][BPh_4]$, the crystal structure of which reveals an O_2^{2-} moiety bound to the rhodium center.[20] In contrast to the latter complex, the neutral compound **3** gives rise to a molecular ion peak in the mass spectrum (FAB). This observation may be explained in terms of the higher electron density at rhodium in **1**, compared with that in $[Rh(P\frown O)_2][BPh_4]$, resulting in an enhanced metal–oxygen bond strength in complex **3**.

As outlined in Scheme III,[16–19] the oxidative addition of methyl iodide to complex **1** shows a pronounced dependence on solvent.[21] Treatment of a solution of **1** in *n*-hexane with MeI results in the formation of a mixture of **5a** and **5b**, the products of a *trans* and *cis* addition, respectively.[22] However, if toluene is used as the solvent, **5b** is generated almost exclusively (*ca.* 95%) along with traces of **5c** as byproduct. This observed solvent effect may be explained on the basis of the assumed intermediates A[23] and B[24] of the oxidative addition, which are similar in energy and thus easily interconvertible (Scheme IV). Coordinating solvents (*e.g.* toluene) preferably interact with species A occupying the vacant coordination site *trans* to the methyl group; attack of iodide can therefore occur only on B, leading to the formation of **5b** and **5c**. In noncoordinating solvents (*e.g.* *n*-hexane), incoming iodide can attack the position either *trans* to methyl (species A) or *cis* to methyl (species B) to give the observed product mixture.

If a solution of **5a** in dichloromethane is warmed to 15 °C, the O,P chelate ring is irreversibly cleaved; **5b** and the new species **5c** can be identified by means of $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR as well as by IR spectroscopy (see Scheme V).

The $^{31}P\{^1H\}$ NMR spectrum of **5a** displays an ABX pattern for the two different phosphine ligands, the chelated one of which resonates at lower field due to its incorporation in a five-membered ring.[25] The analysis of the spectrum yields two different $^1J_{RhP}$ coupling constants (Table II), the smaller value being assigned to the phosphorus atom *trans* to the coordinated ether oxygen atom.[26] The $^2J_{PP}$ coupling constant of 26.9 Hz is characteristic of the *cis* arrangement of the two phosphorus atoms. Likewise, the *cis* position of the phosphine ligands with respect to the methyl group follows from the small $^2J_{PC}$ coupling constants (8.1 and 6.7 Hz) of $^{13}CH_3$-labeled **5a′**.[27] Both **5b** and **5c** give rise to a doublet in the $^{31}P\{^1H\}$ NMR spectrum, which confirms the equivalence of the two phosphines in each complex. The $^{13}CH_3$-enriched compounds **5b′** and **5c′** show ^{13}C chemical shifts of −5.1 and −6.8 ppm for $^{13}CH_3Rh$, respectively,[28] reflecting the

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(16) For simplicity the structures of the complexes **2**, **5b**, and **5c** are depicted as trigonal bipyramids. Complexes of type **6**, however, are reported to adopt rather a square-pyramidal geometry, although distortion has to be envisaged in all cases. See for example refs 17–19.

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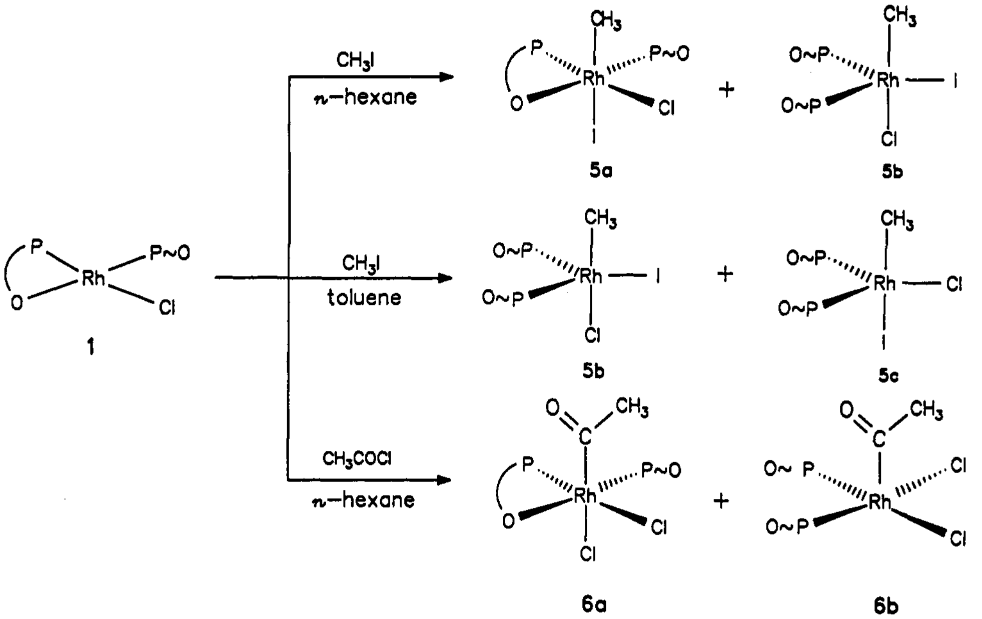
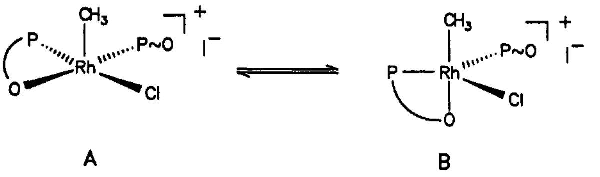
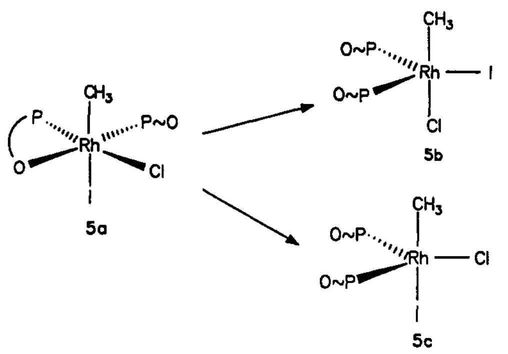
Scheme III



Scheme IV



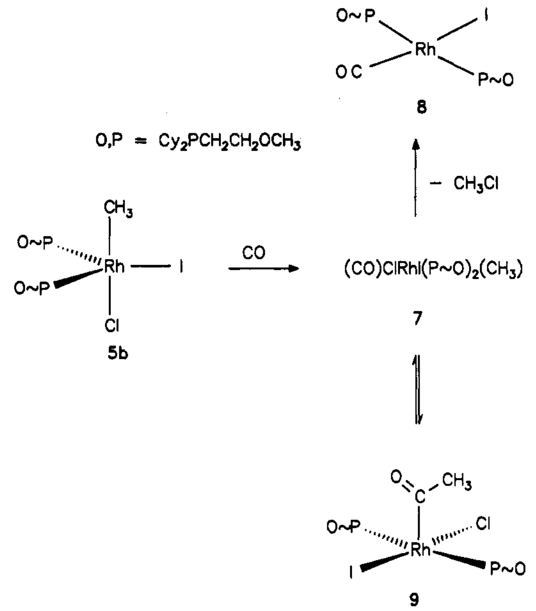
Scheme V



different *trans* influences of Cl^- and I^-.[29] The mass spectrum (FD) of all isomers of 5 consists only of the molecular ion peak, and no diiodo species[30,31] could be detected.

Treatment of 1 with acetyl chloride in *n*-hexene at 0 °C affords a mixture of the acetyl complexes **6a** and **6b** (Scheme III). By analogy with **5a**, **6a** gives rise to an ABX type $^{31}P\{^1H\}$ NMR spectrum, and the $^2J_{PC}$ coupling constants obtained from the $^{13}C\{^1H\}$ NMR spectrum of $^{13}C(O)CH_3$-labeled **6a′** confirm the *cis* position of the acetyl group and the phosphines.[19] The molecular structure of **6b** was assumed on the basis of the magnitude of the $^1J_{RhP}$ coupling constants, which are comparable with that of the related complex *cis*-$[RhCl_2(PPh_3)_2\{C(O)C_2H_5\}]$.[4] The structure of the latter was solved by X-ray structural analysis.

Scheme VI



All IR data are in agreement with the NMR findings. Thus, the coordination of the ether oxygen atom to the rhodium center in **5a** and **6a** leads to a significant shift of $\nu_{as}(C_2O)$ to lower wavelengths (see Table II). As expected, the CO absorptions in the IR spectra of the acetyl complexes **6a** and **6b** appear in the diagnostic range of 1600–1750 cm^{-1}.

The Rh–O bond in 1 is labile and thus easily cleaved by carbon monoxide to give 4 (Scheme II).[13,26] However, the marked oxophilicity of the rhodium(III) center in complex **5a** accounts for the failure of CO to open the O,P chelate ring and the absence of fluxional behavior of the complex. **5b** and **5c** show no propensity to form O,P chelates, an observation which may be attributed to the bulk of the dicyclohexyl(methoxyethyl)phosphine ligand. Steric reasons are also assumed to be the driving force for the conversion of **5a** into **5b** and **5c** upon warming.

Carbonylation of Complex 5b (5b′). Treatment of complex **5b** with carbon monoxide results in the formation of **8** and **9**, both of which were identified by $^{31}P\{^1H\}$ NMR

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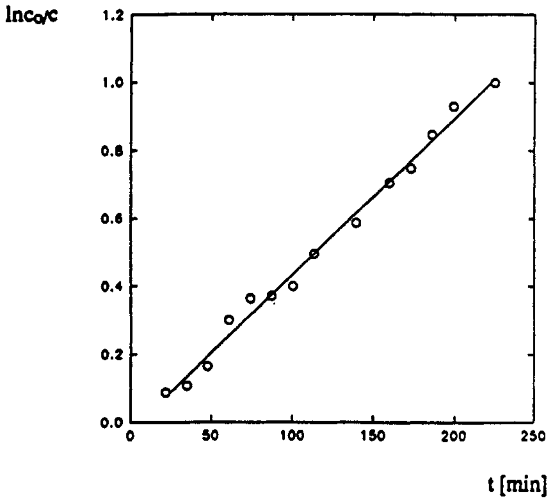

Figure 2. Kinetics plot for the conversion of **5a**′ to **5b**′ and **5c**′ at 287 K (decrease of **5a**′).

spectroscopy (see Scheme VI and Table II). Compound **8** has been reported in the literature,[26] and the structure of **9** was proposed on the basis of $^{31}P\{^1H\}$ NMR data, which correspond to those of the known complex $RhCl_2\{C(O)C_2O_5\}(PPh_3)_2$.[4] Similarly, the ^{13}C-labeled analogue **9**′ was obtained from **5b**′, and its $^{13}C\{^1H\}$ NMR spectrum is in keeping with the above findings. Furthermore, $^{13}CH_3Cl$, which is generated in conjunction with **8**, was unambiguously identified in the reaction medium by means of $^{13}C\{^1H\}$ NMR spectroscopy. Complex **9** is unstable, even at low temperatures, and is quantitatively transformed into **8** at −30 °C over the course of approximately 30 min. As outlined in Scheme VI, the conversion of **9** into **8** is believed to proceed *via* intermediate **7**[22] of hitherto unknown structure. According to IR spectroscopic evidence, however, **7** contains a terminal carbonyl group and is therefore assumed to be a CO adduct of complex **5b**. Species **7** is unstable in solution and rapidly undergoes reductive elimination of CH_3Cl (rather than of CH_3I[32]) to give **8**, accompanied by methyl migration yielding **9**.

Kinetic Study of the Conversion of 5a′ to 5b′ and 5c′. When a solution of complex **5a**′ in $CDCl_3$ is warmed to 287 K, a conversion of **5a**′ to **5b**′ and **5c**′ occurs at a rate which allows the reaction to be conveniently followed by ^{31}P NMR spectroscopy. The analysis of the kinetic data reveals a linear relation between $\ln[c_0/c]$ and time (t) with a correlation coefficient of $R = 0.996$ (c = concentration at time t, c_0 = initial concentration of **5a**′). Hence, the decrease of **5a**′ is first order with a rate constant of $7.67 \times 10^{-5}\ s^{-1}$ at 287 K (see Figure 2).

Conclusion

Complex **1**, which represents an isolable intramolecular solvent complex closely related to the well-known Wilkinson catalyst, shows an excellent catalytic activity in the hydrogenation of 1-hexene to *n*-hexane. An insight into the metal–oxygen bond strength in complexes **1** and **5a**′ has been gained by detailed $^{31}P\{^1H\}$ NMR spectroscopic and kinetic investigations, respectively. As expected, complex **1** is very reactive toward hydrogen, oxygen, methyl iodide, and acetyl chloride.

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