basic rhodo hydrolysis rate enhancement by perchlorate ion.

Although constant ionic strength was not maintained in the perchlorate variation studies at fixed [$OH^-$], a quantitative fit of the rate data to a kinetic expression (eq 2) based on a mechanism (eq 3) that presumes 1:1 ion pairing between the basic rhodo cation

$$k_{\mathrm{obsd}} = k_2 + (k_1 - k_2)/(1 + K_{\mathrm{ip}}[\mathrm{ClO_4^-}]) \qquad (2)$$

$$\mathrm{BR^{4+} + ClO_4^-} \xrightleftharpoons{K_{\mathrm{ip}}} \mathrm{BR^{4+}\cdot ClO_4^-}$$

$$\mathrm{BR^{4+}} \xrightarrow{k_1} \text{products} \qquad (3)$$

$$\mathrm{BR^{4+}\cdot ClO_4^-} \xrightarrow{k_2} \text{products}$$

($BR^{4+}$) and $ClO_4^-$ is instructive. The plausibility of such an ion-pairing scheme is supported by a successful nonlinear least-squares fit[8] of the kinetic data from Table I to eq 2; parameters derived in this manner are $k_1 = (2.14 \pm 0.03) \times 10^{-2}\ s^{-1}$, $k_2 = (3.1 \pm 0.2) \times 10^{-2}\ s^{-1}$, and $K_{ip} = 1.3 \pm 0.6\ M^{-1}$.

As has been pointed out previously,[6] release of ammonia from the basic rhodo cation in alkaline media is more than 3 orders of magnitude faster than the corresponding reaction of $Cr(NH_3)_6^{3+}$ at ambient temperature. It should also be noted that only one $NH_3$ ligand in $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ is exceptionally labile; substitution of the remaining nine ammine ligands in the hydroxo erythro cation is not observed on the stopped-flow time scale. Since a trans effect of the bridging oxide ion cannot account for the cis stereochemistry of the hydroxo erythro product, another source of configurational instability within the basic rhodo ion must be sought. According to a semiquantitative molecular orbital treatment of linear, oxo-bridged Cr(III) dimers,[15,16] the $\pi$-electronic configuration of the basic rhodo ion should be $(e_u^b)^4[(b_{1u})(b_{2g})(e_g)]^6$, where $e_u^b$ is strongly bonding and the remaining MO's are approximately nonbonding (derived from the Cr 3d $t_{2g}$ set) and are in close energetic proximity to one another. Although the ground-state electronic configuration $(e_u^b)^4(b_{1u})^2(b_{2g})^2(e_g)^2$ has been suggested for the basic rhodo ion,[17] alternative distributions of the six nonbonding electrons that could generate a triplet ground term include $(b_{1u})^1(b_{2g})^1(e_g)^4$, $(b_{1u})^1(b_{2g})^2(e_g)^3$, and $(b_{1u})^2(b_{2g})^1(e_g)^3$. Considering the strong temperature dependence of the effective magnetic moment,[18] several of these electronic configurations may contribute under the conditions of our kinetic study and influence the substitution dynamics of an ammonia ligand. The latter two configurations are noteworthy in that $^3E_u$ and $^3E_g$ ground terms would be susceptible to a Jahn-Teller distortion that would necessarily involve bending of the Cr-O-Cr moiety in order to lift orbital degeneracy.[8] Although spectroscopic or magnetic proof is lacking, the hypothesis that a Jahn-Teller distortion required for symmetry reasons provides the "hidden" driving force of the basic rhodo hydrolysis reaction deserves careful consideration and is being explored further in related oxo-bridged, aminechromium(III) dimers. The activation parameters that govern this reaction are consistent with rate-limiting bending of the Cr-O-Cr unit, resulting in loss of $\pi$-bonding, coupled with stretching of the Cr-N bond to the $NH_3$ leaving group.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank a reviewer for bringing ref 13 and 14 to our attention.

**Registry No.** $[(NH_3)_5Cr]_2O^{4+}$, 28050-10-4; $ClO_4^-$, 14797-73-0; $BF_4^-$, 14874-70-5.

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# Synthesis and NMR Characterization of the New Complex *trans*-Dihydridotris((2-methoxyethyl)diphenylphosphine-*P*;-*P*;*O*,*P*)ruthenium(II) with a Reactive Ru-O Bond: Observation of a Low-Energy Exchange Equilibrium[1]

Ekkehard Lindner* and Uwe Schober

*Received June 12, 1987*

Several ruthenium hydrides containing phosphine ligands are known to be potential catalysts for homogeneous hydrogenation processes.[2] During the last few years, increasing attention has been focused on the complex chemistry of "hemilabile" ligands, for example phosphorus-nitrogen,[3] -sulfur,[4] and especially -oxygen[3-6] systems. For ruthenium, interesting results dealing with hybrid ligand halide complexes have been reported,[3,5,6] whereas little work has been done on hydride complexes. As a part of our research in homogeneous catalysis with transition-metal compounds,[6,7] here we report the synthesis and the chemical and spectroscopical properties of the dihydride *trans*-$H_2Ru(\overset{\frown}{PO})(P{\sim}O)_2$ (**2**); $\overset{\frown}{PO}$ designates the chelated, bidentate ligand, while $P{\sim}O$ designates the P-coordinated, $\eta^1$ ligand, with the O functionality not coordinated.

## Experimental Section

All operations were performed under dry, oxygen-free argon,[8] by employing the usual Schlenk techniques. Solvents were dried and stored under argon. IR spectra were recorded with a Bruker IFS 113c Fourier infrared spectrophotometer. Proton-decoupled $^{31}P$ NMR spectra were obtained at 32.391 MHz and $^1H$ NMR spectra at 80.132 MHz with Bruker WP 80 and AC 80 spectrometers. Chemical shifts are in parts per million downfield from 1% $H_3PO_4$/acetone-$d_6$ or from $Me_4Si$, respectively. FD mass spectra were recorded with a Varian MAT 711 A mass spectrometer (8 kV, 50 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; ruthenium was determined with a Perkin-Elmer 4000 atom absorption spectrometer.

**Reagents.** The ruthenium source $RuCl_3\cdot 3H_2O$ was a gift of Degussa AG. The precursor complex $Cl_2Ru(\overset{\frown}{PO})_2$ (**1**)[6] and the ether phosphine ligand $Ph_2PCH_2CH_2OCH_3$[9] were prepared according to literature procedures.

**Preparation of Complex 2.** To a solution of *trans*-$Cl_2Ru(\overset{\frown}{PO})_2$ (**1**) (330 mg, 0.5 mmol) and 1 equiv of $Ph_2PCH_2CH_2OCH_3$ in a hydrogen-saturated mixture of 20 mL of methanol and 50 mL of benzene was added $NaBH_4$ in small portions at 20 °C, until the initial red solution had turned to light yellow. The solvents were removed in vacuo at ambient temperature, leaving a yellow residue. It was suspended in 15 mL of cold (0 °C) methanol and the resulting mixture stirred for 20 min. Filtration (P3) of the suspension gave *trans*-$H_2Ru(\overset{\frown}{PO})(P{\sim}O)_2$ (**2**) as a bright yellow powder; vacuum drying at 20 °C yielded 305 mg (73%) of **2**, mp 47 °C. IR (KBr, $cm^{-1}$): $\nu(RuH_2)$ 1986; $\nu_{as}(C_2O)$ 1092, 1026. $^1H$ NMR (acetone-$d_6$, 20 °C): $RuH_2$ −17.5 ppm (quadruplet; $^2J_{P-H}$ = 25.3 Hz; Figure 1). FD-MS: *m/z* 833, $[M - H_2]^+$. Anal. Calcd for $C_{45}H_{53}O_3P_3Ru$: C, 64.66; H, 6.39; Ru, 12.09. Found: C, 63.89; H, 6.28; Ru, 11.68.

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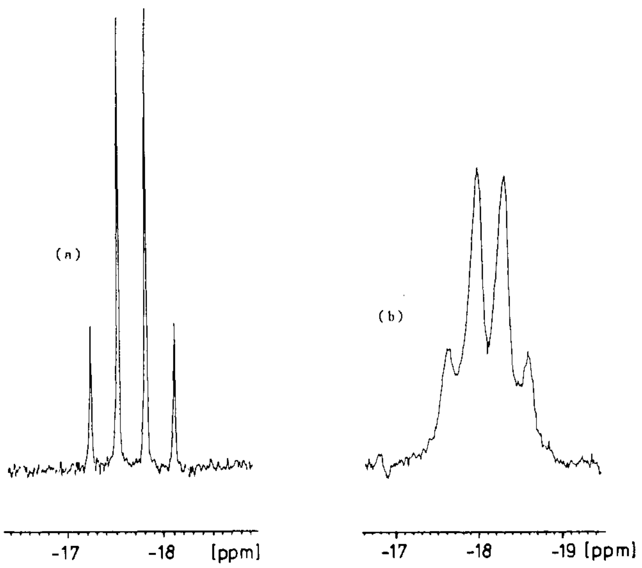
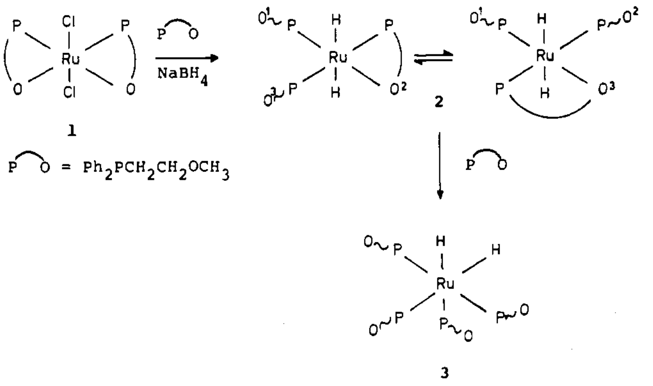


**Figure 1.** High-field hydride region of the 80-MHz $^1$H NMR spectrum of $\mathrm{H_2Ru(P^\frown O)(P{\sim}O)_2}$ (**2**): (a) 24 °C, $^2J_{\mathrm{P-H}} = 25.3$ Hz; (b) -90 °C.

**Scheme I**



$\mathrm{P^\frown O = Ph_2PCH_2CH_2OCH_3}$

**Reaction of 2 with 1 equiv of $\mathrm{Ph_2PCH_2CH_2OCH_3}$.** Addition of $\mathrm{Ph_2PCH_2CH_2OCH_3}$ (122 mg, 0.5 mmol) to a solution of **2** (418 mg, 0.5 mmol) in 20 mL of acetone at 20 °C resulted in formation of the new ruthenium dihydride **3**, characterized in solution by NMR spectroscopy. $^{31}$P{$^1$H} NMR (acetone, -40 °C): 32.2 and 40.1 ppm (triplets, $^2J_{\mathrm{P-P}} = 18.24$ Hz).

## Results and Discussion

Reaction of **1** with $\mathrm{NaBH_4}$ in the presence of 1 equiv of $\mathrm{Ph_2PCH_2CH_2OCH_3}$ in methanol/benzene at ambient temperature results in formation of the yellow hydrido complex **2** in good yields (Scheme I). Complex **2** is rather sensitive toward oxygen, especially in solution. At room temperature, the solid decomposes to a reasonable extent within 2 days even under argon. The $^1$H NMR spectra at two temperatures are shown in Figure 1. The coupling constant of the hydride resonance is typical for cis P-H coupling. We therefore assign trans positions to the two hydride ligands.

$^{31}$P{$^1$H} NMR spectra of **2** are shown in Figure 2. The limiting spectrum is seen at -90 °C. This consists of a regular ABX resonance with a low-field pseudotriplet and an AB spectrum in the higher field region with double the relative intensity. From this spectrum we assign an octahedral structure for **2** with equatorial phosphine ligands and one ruthenium-oxygen contact in the equatorial plane. At this temperature the exchange of O$^2$ and O$^3$ in the coordination to ruthenium is slow enough for the detection of two different P atoms. The pseudotriplet at 57 ppm caused by a phosphine ligand trans to a coordinated ether function of another ligand consists of two doublets at -95 °C (Figure 2) with slightly different coupling constants ($^2J_{\mathrm{P-P}}$ = ca. 32 and 38 Hz), resulting from coupling with two different cis phosphines, one of them acting as a bidentate ligand.

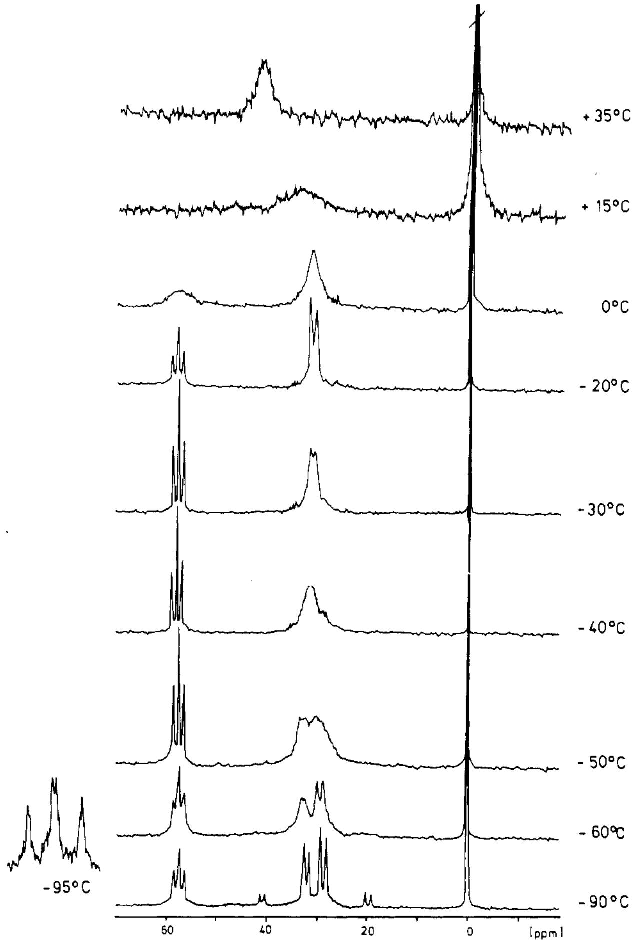


**Figure 2.** Temperature-dependent $^{31}$P{$^1$H} NMR spectra of $\mathrm{H_2Ru(P^\frown O)(P{\sim}O)_2}$ (**2**).

The low-field part of the AB pattern is caused by the chelating ligand; the phosphorus-bonded third ligand with noncoordinating oxygen is responsible for the high-field part. As expected, there are again slightly different cis coupling constants in the A and B parts of the spectrum. A rise in temperature labilizes the chelate system, and the oxygen atoms of both trans ligands now compete for the sixth coordination site. At -40 °C, the exchange of O$^2$ and O$^3$ is fast enough to give a point of coalesence in the spectrum, and at -20 °C, both trans phosphines are equivalent on the NMR time scale (A$_2$X pattern). All three ether phosphine ligands are equivalent at room temperature and thus give rise to one singlet in the $^{31}$P{$^1$H} NMR spectrum. Throughout the whole temperature interval, cis positions of all three phosphorus atoms are relevant for the hydride ligands, the difference in the coupling constants $^2J_{\mathrm{P-H}}$ being too small to be detectable; only at -90 °C does a small effect occur to broaden the hydride quadruplet. At -20 °C, the partially averaged spectrum consists of a regular triplet and a doublet of twice the triplet intensity; the coupling constant $^2J_{\mathrm{P-P}}$ is 34 Hz and is characteristic for cis phosphines in agreement with assignment from the $^1$H NMR spectrum.

The calculated free energy of activation of the exchange process at -40 °C is $\Delta G^\ddagger = 43.7$ kJ/mol,[10] a value much lower than in another comparable case.[11] These results have significant implication for potential catalytic properties; in this context we consider **2** as a protected 16-electron species.

As expected, the IR spectrum of the solid complex **2** is characterized by one absorption for $\nu(\mathrm{RuH_2})$. In the region of $\nu_{\mathrm{as}}(\mathrm{C_2O})$ of the ether side chains (diagnostic for coordinating properties) are two absorptions with relative intensity 2:1. The band for a

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noncoordinating ether function occurs at higher wavenumbers; the less intense band is caused by a chelating ether phosphine.

Complex **2** does not react with $H_2$ at atmospheric pressure,[12] the proton NMR spectrum of the complex dissolved in acetone remaining virtually unchanged after 20 min of hydrogen flushing. However, activation of the ruthenium-oxygen bond proceeds with addition of another 1 equiv of $Ph_2PCH_2CH_2OCH_3$, yielding the hydrido compound *cis*-$H_2Ru(P\sim O)_4$ (**3**). The cis configuration is obvious in the $^{31}P\{^1H\}$ NMR spectrum: two identical triplets for pairs of cis and trans phosphorus nuclei appear.

In conclusion, **2** represents an excellent model complex to demonstrate the opening and closing mechanism of the P,O ligands under very mild conditions.

**Acknowledgment.** We are grateful to the Bundesministerium für Forschung und Technologie, the Deutsche Forschungsgemeinschaft, and the Verband der Chemischen Industrie e. V., Fonds der Chemischen Industrie, for financial support and also to Degussa AG for a gift of $RuCl_3{\cdot}3H_2O$. We thank M. Stängle for NMR measurements.

**Registry No.** **1**, 109011-62-3; **2**, 111557-09-6; **3**, 111557-10-9.

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# Additions and Corrections

1987, Volume 26

**Laurence D. Rosenhein and John W. McDonald***: Synthesis and Characterization of the $[(CO)_4MoS_2MS_2]^{2-}$ and $[(CO)_4MoS_2MS_2Mo(CO)_4]^{2-}$ Ions (M = Mo, W): Species Containing Group VI (6) Metals in Widely Separated Formal Oxidation States.

Page 3414. At the end of the introduction section, we should have quoted the following reference as a prior example of a dinuclear complex containing group 6 metals in widely separated oxidation states: Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1983**, *105*, 5639.—John W. McDonald