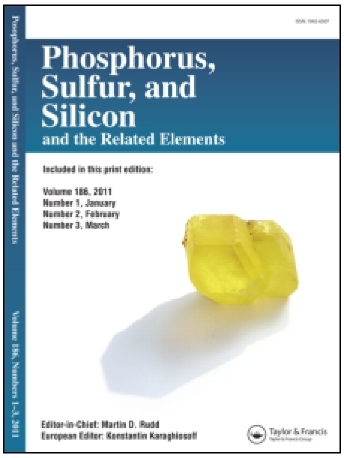

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4-ETHYL-2,6,7-TRIOXA-1-PHOSPHABICYCLO[2.2.2]OCTANE IN COMPLEXING WITH DIRHODIUM(II) TETRAACETATE

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4-ETHYL-2,6,7-TRIOXA-1-PHOSPHABICYCLO[2.2.2]OCTANE IN COMPLEXING WITH DIRHODIUM(II) TETRAACETATE

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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A bicyclic phosphite, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane (I) was used for the complex formation with dirhodium(II) tetraacetate. Under the mole ratio $P/Rh_2 = 2$, the reaction leads to an axial adduct $(AcO)_4Rh_2L_2$. An excess of the phosphite ($P/Rh_2 = 20$) causes the rupture of the metal-metal liaison, reduction of Rh(II) to Rh(I), and formation of a coordinatively unsaturated complex $(RhL_5)^+AcO^-$, which presents a new phenomenon. The complex was identified by low-temperature ^{31}P NMR spectroscopy.

Key words: Bicyclic phosphite, rhodium complexes, religation, ^{31}P NMR spectroscopy.

INTRODUCTION

Binuclear carboxylate complexes of rhodium(II) attract interest because of their electronic structure, reactivity and catalytic features.[1-5] Much attention was paid to the ligand replacement (religation) of these complexes with organophosphorus ligands of various chemical nature. Particular emphasis has been placed on the religation with *tert*-phosphines and phosphites, which resulted usually in the introduction of a phosphorus unit in the axial or equatorial position of the Rh_2^{4+} system.[6-10]‡ Therewith the introduction of the phosphorus ligand in the equatorial position succeeded due to the substitution of only one or two carboxylate groups. We are unaware of any total P(III)-religation of the rhodium(II) coordination sphere to form $[RhL_5]^+$. In this connection it was of interest to investigate the complexing of Rh(II) binuclear complexes with bicyclic phosphites. Such phosphites are upfield P-ligands with low values of steric parameter,[11] and therefore they represent efficient religating agents.[12,13] With regard to the foregoing, we studied the interaction of a typical carboxylate dimeric Rh(II) complex, dirhodium tetraacetate **1**[14] with the most-used bicyclic phosphite, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane **2**.[15]

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‡Note that in the experiments with arylphosphines an ortho-metalation of benzene ring was observed as an auxiliary effect.[10]

RESULTS AND DISCUSSION

The reaction of the initial Rh(II) complex **1** with the bicyclic phosphite **2** in toluene at 20°C and the molar ratio $P/Rh_2 = 2$ results in an axial adduct **3**.

$$\underset{\mathbf{1}}{(AcO)_4Rh_2} + 2\ \underset{\mathbf{2}}{P(OCH_2)_3CEt} \rightarrow \underset{\mathbf{3}}{(AcO)_4Rh_2[P(OCH_2)_3CEt]_2}$$

The yellow complex **3** is stable in the solid state. It is readily soluble in CH_2Cl_2, $C_2H_4Cl_2$, and is chromatographically mobile in a thin silica gel layer. The IR spectrum (KBr) of the compound exhibits characteristic sharp absorptions: ν(POC) 935, 1020; ν_s(COO) 1420; ν_{as}(COO) 1580 cm^{-1}. The ^{31}P NMR spectrum presents a singlet at 58.9 ppm at 30°C (CH_2Cl_2). The calculated coordination shift -34.2 ppm is inherent for complexes of this type.[7] The absence of J(P, Rh) coupling appears to be caused by exchange processes that occur at the experimental temperature. The spectrum becomes more complex when the temperature decreases. The interaction of dirhodium tetraacetate **1** with phosphite **2** to go beyond the formation of axial complex **3** is shown. A complex reorganization of ligands takes place under mole ratio $P/Rh_2 > 2$. With the aim of elucidating the chemical content of the process in question, the complex **1** was treated with a considerable excess of phosphite **2**. The reaction was performed with the mole ratio $P/Rh_2 = 20$ in toluene at 100°C. It was shown that under these conditions an axial P-ligation and a total equatorial P-religation takes place. Furthermore, the process is accompanied by the rupture of a metal-metal bond and the reduction of Rh(II) to Rh(I). (Acetate anion seems to act as reducing agent, see for example Reference 16). Thus a new phenomenon is discovered in the Rh_2^{4+} systems behaviour. In addition, a suitable approach is suggested for the synthesis of pentaphospholigand cationic rhodium complexes $[RhL_5]^+X^-$ hitherto not easily accessible.

$$\underset{\mathbf{1}}{(AcO)_4Rh_2} + 20\ \underset{\mathbf{2}}{P(OCH_2)_3CEt} \rightarrow$$
$$\rightarrow 2\ \underset{\mathbf{4}}{Rh[P(OCH_2)_3CEt]_5AcO} + 10\ \underset{\mathbf{2}}{P(OCH_2)_3CEt}$$

The integration of the ^{31}P NMR spectrum for the reaction mixture enables an easy estimation of the ratio $P/Rh_2 = 5$ in the new complex **4**. The presence of only one sharp signal of complex **4** and that of initial phosphite **2** in the spectrum points to high efficiency of the process (Figure 1).

To prove the structure of the complex **4**, we performed a reverse synthesis involving the reaction of dicarbonylrhodium(I) acetylacetonate **5** with phosphite **2**.[13]

$$\underset{\mathbf{5}}{acacRh(CO)_2} + 10\ \underset{\mathbf{2}}{P(OCH_2)_3CEt} \rightarrow$$
$$\rightarrow \underset{\mathbf{6}}{Rh[P(OCH_2)_3CEt]_5acac} + 5\ \underset{\mathbf{2}}{P(OCH_2)_3CEt}$$

The spectral parameters of the reaction solutions containing the complexes **4** and **6** are identical (Figure 2).

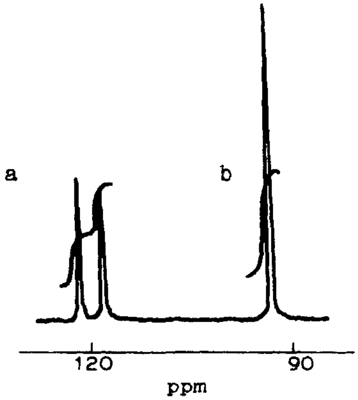

FIGURE 1 ^{31}P NMR spectrum of the reaction solution (AcO)$_4$Rh$_2$ – 20 P(OCH$_2$)$_3$CEt, 30°C, toluene. Complex **4** (a): δ_P 120.0 ppm, ^1J(P, Rh) 182.5 Hz; Phosphite **2** (b): δ_P 93.3 ppm.

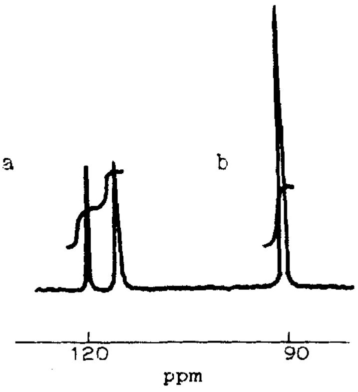

FIGURE 2 ^{31}P NMR spectrum of the reaction solution acacRh(CO)$_2$ – 10 P(OCH$_2$)$_3$CEt, 30°C, CH$_2$Cl$_2$. Complex **6** (a): δ_P 121.0 ppm, ^1J(P, Rh) 182.7 Hz; Phosphite **2** (b): δ_P 93.1 ppm.

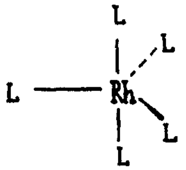

FIGURE 3 Coordinatively saturated trigonal-bipyramidal structure of Rh(I).

The complex **4** was obtained in a colorless solution. Under cooling in air the complex crystallizes slowly. The crystallization is associated with the hydration:

$$\underset{\mathbf{4}}{\mathrm{Rh[P(OCH_2)_3CEt]_5AcO}} + \mathrm{nH_2O} \rightarrow \underset{\mathbf{7}}{\mathrm{Rh[P(OCH_2)_3CEt]_5AcO \cdot nH_2O}}$$

The complex **7** isolated from the solution is a white substance, readily soluble in CH$_2$Cl$_2$, C$_2$H$_4$Cl$_2$, MeOH, H$_2$O. According to the EPR evidence, the complex is

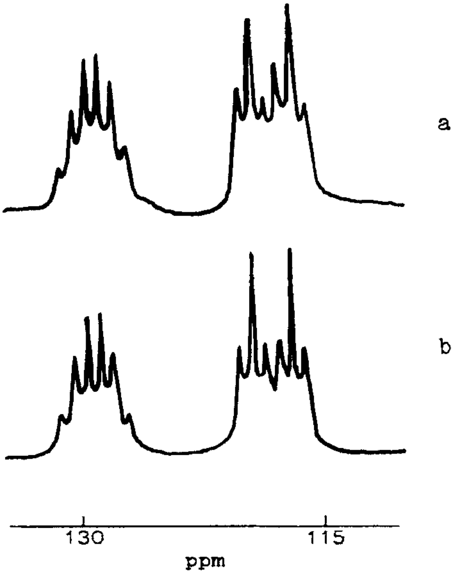

FIGURE 4 Experimental (a) and theoretical (b) $^{31}P\{H\}$ NMR spectra of complex 7. The spectrum (a) is recorded at − 110°C in Freon 122/CD_2Cl_2, 3:1. The spectrum (b) is calculated using Panic program, version 820601.

diamagnetic. The IR spectrum (CH_2Cl_2) presents characteristic absorptions: ν(POC) 930, 1015; ν(COO) 1710 cm^{-1}, as well as absorptions ν(OH) 3300, 3600 cm^{-1}. The water of crystallization was quantitatively determined by a Fisher titration (n = 5). The ^{31}P NMR spectrum presents a doublet at 30°C (see Figure 1): δ_P 121.0 ppm, ^1J(P, Rh) 182.5 Hz (Freon 122/CD_2Cl_2, 3:1). The resonance position represents an average. The averaging is due to the known intramolecular exchange of phosphorus ligands typical for the coordinatively saturated trigonal-bipyramidal structure of Rh(I)[12] (Figure 3).

As the temperature of the complex 7 solution decreases, the pseudo-rotation can be suppressed. Figure 4 shows the compound 7 experimental spectrum (a), which can be described as a doublet of triplets plus a doublet of quadruplets. Indeed, the best correlation with the experimental spectrum is shown by a theoretical spectrum (b) calculated for the model A_2B_3X with the following parameters: $^1J(P_A, Rh)$ 140.1, $^1J(P_B, Rh)$ 209.7, $^2J(P_A, P_B)$ 69.0 Hz, $\Delta\delta_{P_A,P_B}$ 11.5 ppm.

In conclusion it should be noted that the total P-religation reaction of rhodium(II) dimeric complex observed by us is of great importance for an understanding of the nature of metal-metal bond which makes a fundamental unit of many cluster compounds. The elucidation of the phosphorus ligand effect on the Rh—Rh bond rupture can be helpful for controlling composition of the cluster rhodium complexes resultant in the metallocomplex catalysis processes.

EXPERIMENTAL

Infrared spectra were recorded on a Specord M80 instrument. ^{31}P NMR spectra were recorded with a Bruker CXP-200 at 81 MHz (vs 85% H_3PO_4 in D_2O as external standard).

Phosphite **2**,[15] complex **1**,[17] and compound **6**[13] were prepared according to the procedures reported in the literature.

Synthesis of complex **3**. A reaction mixture containing 2.5×10^{-4} mole of complex **1** and 5×10^{-4} mole of phosphite **2** in 50 mL of toluene was stirred vigorously to the total dissolving of compound **1**. The orange solution was evaporated to a volume of 5 mL and cooled. A yellow complex was filtered off, washed with hexane and dried. Yield 60%, m.p. > 183°C (dec.), R_f 0.3 (Silufol UV-254, benzene/dioxane, 5:1).

Preparation of complex **7**. A reaction mixture containing 2.5×10^{-4} mole of complex **1** and 5×10^{-3} mole of phosphite **2** in 5 mL of freshly distilled toluene was heated to 100°C in a sealed glass tube until it decolorizes. Once cooled, the tube was opened to the air. The solvent was evaporated, and the residue was washed with ether and filtered. The complex on the filter was washed with an additional portion of ether to remove an excess of phosphite. The purity was confirmed by ^{31}P NMR spectroscopy. Complex **7** constitutes fine white crystals. Yield 95%, b.p. > 185°C (dec). Found: C, 36.25, H, 6.24, P, 14.32, H_2O 8.50. $C_{32}H_{68}O_{22}P_5Rh$ calcd.: C, 36.16, H, 6.40, P, 14.60, H_2O, 8.48%.

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