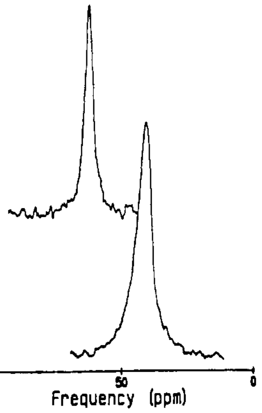

Figure 5. Spectra of water at 50 mM (top) and 200 mM (bottom) concentrations in a 0.8:1.0 melt ($AlCl_3$/ImCl).

a solution of water in a basic melt is to shift the peak upfield. These results suggest that fast chemical exchange is taking place between two or more oxygen environments, probably "Al–O" and "Al–OH" moieties. The "Al–OH" species presumably has a smaller chemical shift value than the "Al–O" species, thus explaining the behavior upon addition of HCl. The observed concentration dependence then indicates that the "Al–O" moiety is the predominant oxide environment at low concentrations while "Al–OH"-containing species are more important at higher concentrations. This suggests that the discrepancy between the infrared[7] and electrochemical[9] results is due to the higher water concentrations used in the former case relative to those typically employed in the neutral-melt amperometric titration technique utilized in the latter case. These results also provide direct evidence for the type of equilibrium used to explain the behavior of the Ti(IV) system upon addition of H_2O. In the latter experiment, relatively large H_2O concentrations were added to the titanium solutions.

In conclusion, ^{17}O studies have enabled us to deduce the nature of the speciation in H_2O solutions in melts. In acidic melts, three oxygen-containing species are formed: one hydroxochloroaluminate and two O-bridged oxochloroaluminate species. In basic melts, rapid exchange precludes determination of the exact number of species formed, but we can qualitatively conclude that an oxochloroaluminate, probably in a terminal environment, and a hydroxochloroaluminate are present, with the latter species being the predominant form at high water concentrations.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research.

Registry No. H_2O, 7732-18-5; $AlCl_3$, 7446-70-0; 1-methyl-3-ethylimidazolium chloride, 65039-09-0.

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Rhodium(I) Production during the Oxidation by Water of a Hydrosoluble Phosphine

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Received November 13, 1986

Water-soluble and hydrophilic phosphines have been synthesized recently[1-8] to accord water solubility to homogeneous catalysts, affording a means to separate them from organic products in biphasic (water and organic phase) systems. We here report our studies of the highly hydrosoluble trisodium phosphinetriyltri-*m*-benzenesulfonate, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$, patented by Rhône-Poulenc S.A.[1] We have prepared hydrosoluble rhodium(I) coordination compounds such as $RhCl(TPPTS)_3$ by reacting TPPTS on a Rh(I) precursor under carefully controlled reaction conditions.[9] But attempts to synthetize the persulfonated analogue of Wilkinson's complex from $RhCl_3$ have failed because we have found that this hydrosoluble phosphine is readily oxidized by Rh(III) in water in the absence of oxygen. In this paper we show that a redox process occurs between rhodium(III), TPPTS, and water. The production of phosphine oxide is accompanied by the formation of Rh(I) characterized by its coordination complexes with the sulfonated phosphine.

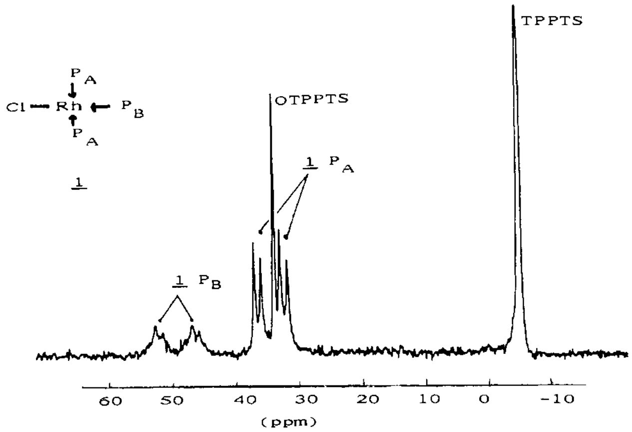

Figure 1. 32.38-MHz $^{31}P\{^1H\}$ NMR spectrum of $RhCl_3{\cdot}3H_2O$ and 3 equiv of TPPTS after 21 h (P_A and P_B = TPPTS).

Table I. ^{31}P NMR Data in Water

complex	$\delta(P)^{a,b}$	J_{Rh-P}, Hz	$J_{P_A-P_B}$, Hz
1 (H_2O, 36 °C)	34.6 (P_A)	142 (P_A)	39
	50.7 (P_B)	195 (P_B)	
$RhCl(PPh_3)_3$ (CH_2Cl_2, 28 °C)[10]	32.2 (P_A)	146 (P_A)	38
	48.9 (P_B)	192 (P_B)	

[a] P_A represents the two equivalent phosphorus atoms trans to each other. P_B is the phosphorus atom trans to the halogen. [b] External reference H_3PO_4 85%.

Results

^{31}P NMR Studies. When 3 equiv of TPPTS and 1 equiv of $RhCl_3$ are dissolved in scrupulously deaerated water and allowed to react under nitrogen at room temperature, the ^{31}P NMR spectrum of the reaction mixture recorded after 21 h reveals the presence of $O{=}P(PhSO_3Na)_3$ (OTPPTS), of unreacted phosphine and of $RhCl(TPPTS)_3$ (**1**) (Figure 1).[9] Structure **1** has been assigned by comparison of the data obtained in water with those of the triphenylphosphine complex (Table I).

This experiment demonstrates that rhodium(III) has been partially reduced and trapped by TPPTS (approximately 50% of the rhodium introduced is characterized in the rhodium(I) complex 1) and that oxidation of TPPTS occurs at the same time even in the absence of oxygen. The amount of rhodium(I) and phosphine

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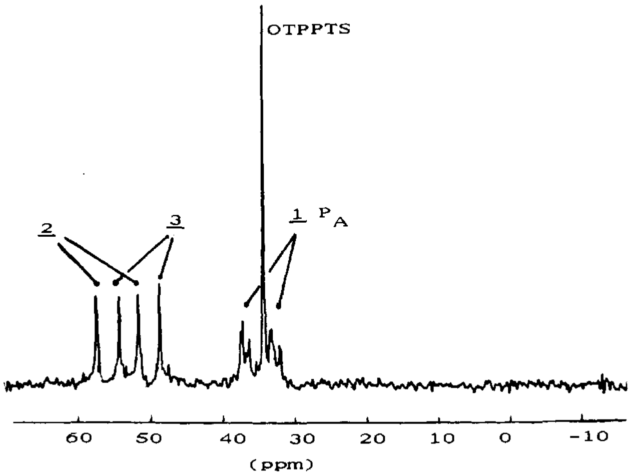


Figure 2. 32.38-MHz ^{31}P {^{1}H} NMR spectrum of $RhCl_3 \cdot 3H_2O$ and 1 equiv of TPPTS after 50 min.

Table II. ^{31}P NMR Coupling Constants

complex	J_{Rh-P}, Hz	complex	J_{Rh-P}, Hz
RhCl(TPPTS)$_2$ (**2**)	200 (δ = 55.3)	(RhCl(PCy$_3$)$_2$)$_2$[11]	194
(RhCl(TPPTS)$_2$)$_2$ (**3**)	195 (δ = 52.1)	(RhCl(PPh$_3$)$_2$)$_2$[12,a]	193 (δ = 51.9)
RhCl(PCy$_3$)$_2$[11]	210		

[a] The monomer RhCl(PPh$_3$)$_2$ has never been characterized by ^{31}P NMR spectroscopy; its formation by flash photolysis is described in a recent publication.[26]

oxide produced in a given period of time depends on the ratio R = TPPTS/RhCl$_3$. For instance, when R = 1, the rate of production of rhodium(I) and OTPPTS is considerably increased. The ^{31}P NMR spectrum recorded after 10 min under nitrogen shows that 21% of the phosphine is oxidized and that 19% of the rhodium has been reduced and trapped by TPPTS to afford complex **1**. Forty minutes later the reaction mixture does not contain unreacted phosphine; the ^{31}P NMR spectrum also reveals an increase in the amount of phosphine oxide and rhodium(I). In the meantime partial transformation of **1** into the monomeric species **2** and the corresponding dimer **3** has occured (Figure 2). The two doublets at δ = 55.3 and 52.1 are respectively attributed to **2** (RhCl(TPPTS)$_2$) and **3** ([RhCl(TPPTS)$_2$]$_2$); these coordination compounds are identified by comparison of their spectroscopic data (particularly the values of rhodium–phosphorus coupling constants) with those of known organosoluble analogues (Table II). Further recordings show an equilibrium between **2** and **3**.

On the contrary, when R = 10, the oxidation rate and the amount of rhodium(I) detected are considerably reduced. After 10 h the mixture still contains 90% unreacted TPPTS and the amounts of phosphine oxide and rhodium(I) in complex **1** are very low and correspond respectively to 4% and 6% of the phosphorus.

Labeling Experiments. These ^{31}P NMR experiments clearly demonstrate that a redox reaction occurs in water between Rh(III) and the hydrosoluble phosphine because the results described are obtained under anaerobic conditions. It is obvious that water must be the source of oxygen during the redox reaction.

The oxidation of TPPTS by water is proved by the labeling of the oxide produced when the reaction is performed in $^{18}OH_2$ (isotopic purity 98.2%). Field desorption mass spectrometry shows that 55% of the oxide has been labeled by ^{18}O. The remaining 45% of unlabeled phosphine oxide originates from two sources: the rhodium trichloride hydrated used contains $^{16}OH_2$ and at the end of the reaction oxygen is inevitably introduced.

Discussion

Table III. Production of OTPPTS and Rh(I)

		reacn time 1 h and 30 min		reacn time 2 h and 30 min	
no.	expt	% OTPPTS	% Rh(I)	% OTPPTS	% Rh(I)
1	RhCl$_3$/3TPPTS; NaCl 2 M	4	1[a]	5	6[a]
2	RhCl$_3$/3TPPTS; HClO$_4$ 0.5 M	10	9[a]	12	11[a]
3	RhCl$_3$/3TPPTS; H$_2$O	57	64[b]	70	44[b]

[a] Complex **1**. [b] Complexes **2** and **3**.

The redox reaction between water, rhodium(III), and TPPTS bears analogies with other experiments on the hydration of alkenes or alkynes[13,14] or on the water gas shift.[15] In some cases,[13,14] a transient hydroxyrhodium(III) intermediate has been postulated. Our study brings evidences that an hydroxydichlororhodium intermediate, formed via eq 1, plays a major role in this redox process.

$$RhCl_3 + H_2O \rightleftharpoons RhCl_2(OH) + H^+ + Cl^- \qquad (1)$$

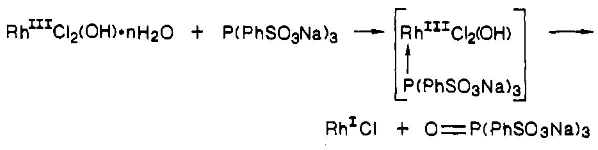
The existence of RhCl$_2$(OH) in a solution obtained by addition of $RhCl_3 \cdot 3H_2O$ to deaerated water is confirmed by an ^{1}H NMR study. The two signals at –0.16 and –0.19 ppm can be attributed to the *fac* and *mer* Rh(III) isomers of $RhCl_2(OH) \cdot 3H_2O$; similar chemical shifts have been measured for some Rh and Ru hydroxylated species.[16-18]

Moreover, hydrolysis of rhodium trichloride in water is supported by the rapid increase of acidity accompanying its dissolution. Then the stabilization of pH is in agreement with the equilibrium of eq 1.

Numerous papers have been devoted to the behavior of rhodium(III) in water, and a large amount of data concerning the nature of the solvated species and the equilibria existing between them are available.[19-24] These experiments have been conducted in acidic media and under conditions of controlled ionic strength. Such conditions inhibit the formation of hydroxy species.[19]

Indeed, oxidation of the phosphine and reduction of rhodium(III) depend on the factors that influence equilibrium 1. For instance when rhodium trichloride was added to a water solution of TPPTS either at low pH value (HClO$_4$ 0.5 M) or at high chloride concentration (NaCl 2 M) we found that the rates of OTPPTS and Rh(I) production are very slow even in the presence of oxygen (Table III).

The redox process that we have discovered starts by the hydrolysis of RhCl$_3$ (eq 1) and can be revealed because the highly hydrosoluble phosphine readily reacts with RhCl$_2$(OH) (eq 2).



$$Rh^{III}Cl_2(OH) \cdot nH_2O + P(PhSO_3Na)_3 \longrightarrow \left[\begin{array}{c} Rh^{III}Cl_2(OH) \\ \uparrow \\ P(PhSO_3Na)_3 \end{array}\right] \longrightarrow Rh^{I}Cl + O{=}P(PhSO_3Na)_3 \qquad (2)$$

The coordination step is certainly important, but the driving force of the reaction leading to the production of rhodium(I) is brought by the oxidizability of TPPTS. When enough phosphine is present,

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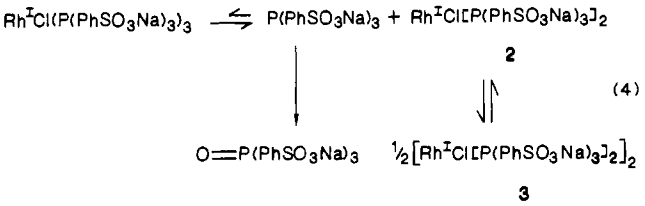
Rh(I) is trapped to afford complex **1** (eq 3). Then compound

$$\mathrm{Rh^ICl} + 3\mathrm{P(PhSO_3Na)_3} \rightarrow \underset{\mathbf{1}}{\mathrm{Rh^ICl[P(PhSO_3Na)_3]_3}} \quad (3)$$

1 can dissociate with liberation of phosphine and production of the coordinatively unsatured compound **2**, which dimerizes (eq 4).



The rate of oxidation strongly depends on the concentration of TPPTS as can be expected by the existence of several equilibria in solution. It must be noticed that without rhodium reoxidation the amount of phosphine oxide produced cannot exceed the molarity of the metal. The catalytic oxidation of TPPTS will be discussed in another paper. Finally other transition metals in high oxidation states are able to perform the same kind of redox reaction in water; our preliminary studies with $RuCl_3{\cdot}3H_2O$ lead to the same observations.

Conclusion

The major observation from this study is that a highly reactive hydroxyrhodium(III) species, formed when rhodium trichloride is dissolved in water, is responsible for the oxidation of the hydrosoluble phosphine used. Labeling experiments prove that water is decomposed and is the source of oxygen. These findings are of interest for the development of transition metal chemistry in water and also from a practical point of view because the sacrifice of some hydrosoluble phosphines affords metal salts in a low oxidation state, which may prove useful for the generation of catalytically active species.

Experimental Section

Starting Materials. $RhCl_3{\cdot}3H_2O$, TPPTS, and $H_2{}^{18}O$ (98.2%) were respectively supplied by Janssen, Rhône-Poulenc and CEA (Service des Molécules Marquées).

The ^{31}P NMR spectra were recorded at 36 °C on a Brucker WP 80-MHz instrument, and the ^1H NMR spectrum was obtained by using a Brucker AM 300-MHz instrument with irradiation of water.

^{31}P NMR Study of a Deaerated Aqueous Solution of TPPTS and $RhCl_3{\cdot}3H_2O$ (Molar Ratio 3/1). A mixture of 53 mg of $RhCl_3{\cdot}3H_2O$ (0.2 mmol) and 365 mg of TPPTS (0.6 mmol) is dissolved in 2 mL of deaerated distilled water. The ^{31}P NMR spectrum is recorded after 21 h under nitrogen at room temperature: $\delta = -5.5$ (s), 28%, TPPTS; $\delta = 34.1$ (s), 21%, OTPPTS; $\delta = 34.6$, $J_{Rh-P_A} = 142$ Hz, $J_{P_A-P_B} = 39$ Hz (dd), $\delta = 50.7$, $J_{Rh-P_B} = 195$ Hz, $J_{P_A-P_B} = 39$ Hz (dt), 51%, $RhCl(TPPTS)_3$ (**1**).

^{31}P NMR Study of a Deaerated Aqueous Solution of TPPTS and $RhCl_3{\cdot}3H_2O$ (Molar Ratio 1/1). A mixture of 46 mg of $RhCl_3{\cdot}3H_2O$ (0.18 mmol) and 110 mg of TPPTS (0.18 mmol) is dissolved in 2 mL of deaerated distilled water. The ^{31}P NMR spectrum is recorded after 10 min under nitrogen at room temperature: $\delta = 34.5$ (s), 21%, OTPPTS; $\delta = 34.6$, $J_{Rh-P_A} = 143$ Hz, $J_{P_A-P_B} = 40$ Hz (dd), δ 50.5, $J_{Rh-P_B} = 198$ Hz, $J_{P_A-P_B} = 40$ Hz (dt), 58%, $RhCl(TPPTS)_3$ (**1**); $\delta = -5.5$ (s), 21% TPPTS.

The ^{31}P NMR spectrum recorded 40 min later shows the following data: $\delta = 34.2$ (s), 29% OTPPTS; $\delta = 34.6$, $J_{Rh-P_A} = 142$ Hz, $J_{P_A-P_B} = 40$ Hz (dd), 28%, $RhCl(TPPTS)_3$; $\delta = 55.3$, $J_{Rh-P} = 200$ Hz (d), 21%, $RhCl(TPPTS)_2$ (**2**); $\delta = 52.1$, $J_{Rh-P} = 195$ Hz (d), 22%, $[RhCl(TPPTS)_2]_2$ (**3**). The intense signals of **2** and **3** do not allow the observation of the resonance of the atom P_B (trans to halogen) in complex **1**.

^{31}P NMR Study of a Deaerated Aqueous Solution of TPPTS and $RhCl_3{\cdot}3H_2O$ (Molar Ratio 1/10). A mixture of 17 mg (0.06 mmol) of $RhCl_3{\cdot}3H_2O$ and 385 mg (0.6 mmol) of TPPTS is dissolved in 2 mL of deaerated water. The ^{31}P NMR spectrum is recorded after 10 h under nitrogen at room temperature: $\delta = -5.5$ (s), 90%, TPPTS; $\delta = 33.9$ (s), 4%, OTPPTS; $\delta = 34.6$, $J_{Rh-P_A} = 142$ Hz, $J_{P_A-P_B} = 39$ Hz (dd), $\delta = 50.6$, $J_{Rh-P_B} = 191$ Hz, $J_{P_A-P_B} = 39$ Hz (dt), 6%, $RhCl(TPPTS)_3$ (**1**).

^{1}H NMR Study of an Aqueous Solution of $RhCl_3{\cdot}3H_2O$. A 100-mg sample of $RhCl_3{\cdot}3H_2O$ is dissolved under nitrogen in a deaerated mixture of distilled water (1.6 mL) and CD_3COCD_3 (0.4 mL). The ^1H NMR spectrum is recorded on a Brucker AM 300 MHz with water irradiaton: $\delta = -0.16$ (br), $\delta = -0.19$ (br), relative intensity 1/1.

pH of an Aqueous Solution of $RhCl_3$. A 100-mg sample of $RhCl_3{\cdot}3H_2O$ is dissolved in 60 mL of distilled and deaerated water ($[RhCl_3] = 6.3 \times 10^{-3}$ M) in an electrochemical cell equipped with a satured calomel electrode and a glass electrode. The pH value decreases quickly from 7.2 (distilled water) to 2.6 after 10 min and then stabilizes at 2.5 after 3 h.

Labeling Experiment. A mixture of 87 mg of $RhCl_3{\cdot}3H_2O$ (0.33 mmol) and 203 mg of TPPTS (0.33 mmol) is dissolved under nitrogen in 1 mL of deaerated $^{18}OH_2$ (isotopic purity 98.2%); the mixture is kept at room temperature for 7 days under an inert atmosphere. An excess of water is removed under vacuum and the product is dried at 80 °C. Analysis of the sample with a field desorption mass spectrometer was realized at Rhône-Poulenc Décines. Two molecular ions are observed: m/z 561 (^{16}OTPPTS, 45%), 563 (^{18}OTPPTS, 55%). The ^{31}P NMR spectrum shows one singlet at $\delta = 33.9$ (85%, OTPPTS) and two doublets respectively at $\delta = 35.4$ ($J_{Rh-P} = 124$ Hz, 11%) and 34.5 ($J_{Rh-P} = 122$ Hz, 4%) attributed to rhodium(III) complexes by comparison with literature data for $ClRh(OH)(acac)(PPh_3)$.[25]

Influence of H$^+$ or Cl$^-$ Concentration on the Redox Reaction. A mixture of 42 mg (0.16 mmol) of $RhCl_3{\cdot}3H_2O$ and 280 mg (0.46 mmol) of TPPTS is dissolved in 2 mL of an aqeuous solution of NaCl (2 M) (experiment no. 1), in 2 mL of an aqueous solution of $HClO_4$ (0.5 M) (experiment no. 2), or in 2 mL of distilled water (experiment no. 3). Solutions 1–3 are kept in the NMR tubes without precautions. The ^{31}P NMR spectra are recorded after 1 h and 30 min and 2 h and 30 min. The amounts of OTPPTS and Rh(I) formed are listed in Table III.

Acknowledgment. We thank Rhône-Poulenc Recherches (Centre de Recherches de Saint-Fons) for generous loans of TPPTS and C.L. gratefully acknowledges Rhône-Poulenc S.A. for a grant and P. Lecomte for the mass spectra and discussions.

Registry No. **1**, 109584-77-2; **2**, 109584-78-3; **3**, 109584-79-4; TPPTS, 63995-70-0; OTPPTS, 98511-67-2; $RhCl_3$, 10049-07-7; H_2O, 7732-18-5.

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Additions and Corrections

1985, Volume 24

Gary M. Gray* and Keith A. Redmill: Correlations between the Taft E_s Parameters and ^{13}C Chemical Shifts in $Mo(CO)_4((Ph_2PO)_2Si(Me)R)$ (R = Alkyl) Complexes. A New Method for the Measurement of Taft E_s Parameters.

Page 1280. The $|^1J(PC) + {}^3J(P'C)|$ values for C(1) that are reported in Table I are one-half of the correct values.—Gary M. Gray

1986, Volume 25

Gary M. Gray,* Alan L. Zell, and Howard Einspahr: Synthesis and Structure of *trans*-Bis[[pentacarbonyl(*N*-(2-((diphenylphosphino)amino)ethyl)salicylaldiminato-*P*)]molybdenum(0)-*N*,*O*]copper(II): A Novel Trimetallic Complex with a Mixed P-Donor–Schiff-Base Bridging Ligand.

Page 2923. The correct space group for the complex is $P\bar{1}$ and not $P1$ as given in the third line of the third paragraph.—Gary M. Gray