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Studies on Metal Carboxylates.
XV [1]. Solution Reactions of Rhodium(II) Acetate with the Gaseous Hydrogen Halides. The Formation of Complexes of Rhodium(III)

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Rhodium(II) acetate, $Rh_2(O_2CCH_3)_4$, reacts with gaseous HCl and HBr in acetone or ethanol to produce an insoluble residue of rhodium metal and solutions containing rhodium(III) which, upon treatment with $Ph_4AsCl \cdot nH_2O$, produce the salts $(Ph_4As)RhCl_4(H_2O) \cdot H_2O$ and $(Ph_4As)RhBr_4(H_2O)$. These can in turn be used as starting materials for the synthesis of a variety of new rhodium(III) species. Complexes prepared in the present work are $(Ph_4As)RhX_4(CH_3CN)$, $RhX_3(PPh_3)_2(CH_3CN)$ and $[RhX_2(LL)_2]X \cdot 2EtOH$, where LL = 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylarsino)ethane. Details of their synthesis and spectral characterization are described. The X-ray photoelectron spectra (XPS) of $[RhX_2(LL)_2]X \cdot 2EtOH$ show that the Cl 2p and Br 3p binding energies of the inner and outer sphere halogen environments differ by between 1.3 and 1.7 eV. The reactions of $Rh_2(O_2CCH_3)_4$ with HX(g) in non-aqueous media are contrasted with the corresponding reactions of the solid acetate with HX(g).

Introduction

In our search for synthetic routes to the elusive rhodium(II) halides [2], we have explored the possibility of using rhodium(II) acetate, $Rh_2(O_2CCH_3)_4$, as a synthetic starting material. Since molybdenum(II) acetate, $Mo_2(O_2CCH_3)_4$, reacts with the gaseous hydrogen halides (HCl, HBr and HI) to afford the β-MoX_2 phases [3, 4], it seemed possible that the displacement of the acetate groups from $Rh_2(O_2CCH_3)_4$ might, in a similar fashion, produce RhX_2. Although products of composition approximating to RhX_2 were indeed formed upon reacting solid $Rh_2(O_2CCH_3)_4$ with gaseous HCl, HBr and HI at 300–340 °C [3, 5], characterization of these materials showed them to be mixtures of rhodium metal and the appropriate rhodium(III) halide [3, 5]. Two possible reactions could account for these observations: (1) the thermal disproportionation of RhX_2, *i.e.*, $3RhX_2 \xrightarrow{300\,°C} Rh + 2RhX_3$ and, (2) the reaction of the unstable dihalides with excess of hydrogen halide, *i.e.*, $2RhX_2 + 2HX \xrightarrow{300\,°C} RhX_3 + H_2$. Since the course of the reactions between $Rh_2(O_2CCH_3)_4$ and HX should be strongly influenced by the reaction conditions, we have subsequently explored the reactions of this acetate both with liquid HX at low temperatures [5] and with gaseous HX in non-aqueous solvents. The results of the latter of these two studies are now communicated.

Experimental

Starting Materials

Rhodium(II) acetate was prepared from $RhCl_3 \cdot 3H_2O$ using the established procedure [6, 7] and isolated as the methanolate $Rh_2(OAc)_4 \cdot nMeOH$. All other starting materials were available from commercial sources and were used as received.

Synthetic Procedures

$(Ph_4As)RhCl_4 \cdot 2H_2O$

$Rh_2(OAc)_4 \cdot nMeOH$ (0.2 g) was added to 35 ml of dry, deoxygenated acetone and nitrogen gas bubbled through the solution for 15 minutes. The nitrogen flow was replaced by HCl gas which was continuously bubbled into the solution while it refluxed for 1 hour. The solution was then allowed to cool and nitrogen gas used to flush out the HCl. After filtering the solution, $Ph_4AsCl \cdot xH_2O$ (0.5 g) dissolved in 5 ml of ethanol was added and the reaction mixture cooled to 0°. After 2 days, the solution was filtered, and the brown $(Ph_4As)RhCl_4 \cdot 2H_2O$ (0.18 g) collected, washed with acetone and diethyl ether, and dried in vacuo. *Anal.* Calcd. for $C_{24}H_{24}AsCl_4O_2Rh$: C, 43.39; H, 3.62; Cl, 21.36. Found: C, 42.67; H, 3.73; Cl, 21.31.

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$(Ph_4As)RhBr_4 \cdot H_2O$

$Rh_2(OAc)_4 \cdot nMeOH$ (0.2 g) was added to 25 ml of dry, deoxygenated ethanol and nitrogen gas bubbled through the solution for 15 minutes. The reaction mixture was then refluxed for 20 minutes while a stream of HBr gas was bubbled through it. The reaction mixture was cooled to room temperature, nitrogen gas used to flush out the excess HBr gas and the solution was then filtered. $Ph_4AsCl \cdot xH_2O$ (0.6 g), dissolved in 5 ml of ethanol, was added to the filtrate, which was then refrigerated at 0° for 2 days. The resulting dark brown complex $(Ph_4As)RhBr_4 \cdot H_2O$ (0.4 g) was filtered off, washed with ethanol, diethyl ether, and dried in vacuo. *Anal.* Calcd. for $C_{24}H_{22}AsBr_4ORh$: C, 34.96; H, 2.67; Br, 38.83. Found: C, 34.85; H, 2.73; Br, 39.47.

$(Ph_4As)RhX_4 \cdot CH_3CN$ (X = Cl or Br)

$(Ph_4As)RhX_4 \cdot xH_2O$ (~0.17 g) was added to 20 ml of dry, deoxygenated acetonitrile and stirred until all had dissolved. The red solution was then evaporated to dryness and the salmon pink solid collected. *Anal.* Calcd. for $C_{26}H_{23}AsCl_4NRh$: C, 46.65; H, 3.44; Cl, 21.20; N, 2.09. Found: C, 46.56, H, 3.66; Cl, 20.73; N, 2.33; yield, 40%. *Anal.* Calcd. for $C_{26}H_{23}AsBr_4NRh$: C, 36.84; H, 2.72; Br, 37.78. Found: C, 36.50; H, 2.86; Br, 37.26; yield, 50%.

$RhCl_3(PPh_3)_2(CH_3CN)$

$(Ph_4As)RhCl_4 \cdot 2H_2O$ (0.15 g) and triphenylphosphine (0.15 g) were added to 15 ml of dry, deoxygenated acetonitrile and the reaction mixture refluxed while continually being stirred. After 2 hours the solution was cooled and the orange crystals of $RhCl_3(PPh_3)_2(CH_3CN)$ (0.1 g) collected, washed with acetonitrile, ethanol, diethyl ether, and dried in vacuo. Yield: 57%. *Anal.* Calcd. for $C_{38}H_{33}Cl_3NP_2Rh$: C, 58.89; H, 4.29; Cl, 13.73; N, 1.81. Found: C, 58.41; H, 4.53; Cl, 13.36; N, 2.00.

$RhBr_3(PPh_3)_2(CH_3CN)$

Using a similar procedure to the preceding one, the orange $RhBr_3(PPh_3)_2(CH_3CN)$ was collected after refluxing for 1 day. Yield: 30%. *Anal.* Calcd. for $C_{38}H_{33}Br_3NP_2Rh$: C, 50.22; H, 3.63; Br, 26.43. Found: C, 50.49; H, 3.46; Br, 26.00.

$[RhCl_2(dppe)_2]Cl \cdot 2EtOH$

$(Ph_4As)RhCl_4 \cdot 2H_2O$ (0.17 g) and 1,2-bis(diphenylphosphino)ethane (0.3 g) were added to 25 ml of dry, deoxygenated ethanol. The reaction mixture was refluxed and stirred for 2 days. It was then filtered while hot and the filtrate refrigerated overnight. The yellow crystalline complex (0.08 g), whose composition approximated to that of the ethanol solvate, $[RhCl_2(dppe)_2]Cl \cdot 2EtOH$, was then collected, washed with ethanol, benzene, diethyl ether, and dried in vacuum. Yield: 30%. *Anal.* Calcd. for $C_{56}H_{60}Cl_3O_2P_4Rh$: C, 61.24; H, 5.47; Cl, 9.69. Found: C, 59.41; H, 5.24; Cl, 9.33.

Procedures similar to the preceding one were used to prepare $[RhCl_2(dpae)_2]Cl \cdot 2EtOH$, as well as the analogous bromide complexes $[RhBr_2(dppe)_2]Br \cdot 2EtOH$ and $[RhBr_2(dpae)_2]Br \cdot 2EtOH$. *Anal.* Calcd. for $C_{56}H_{60}As_4Cl_3O_2Rh$: C, 52.77; H, 4.63; Cl, 8.35. Found: C, 52.55; H, 4.51; Cl, 8.43. Calcd. for $C_{56}H_{60}Br_3O_2P_4Rh$: C, 54.59; H, 4.87. Found: C, 54.17; H, 5.04. Calcd. for $C_{56}H_{60}As_4Br_3O_2Rh$: C, 47.76; H, 4.26; Br, 17.06. Found: C, 47.76; H, 4.26; Br, 16.58.

Physical Measurements and Analytical Procedures

These were carried out as described previously [3].

Results and Discussion

Rhodium(II) acetate reacts with gaseous HCl and HBr to afford solutions which, upon treatment with an excess of $Ph_4As^+Cl^-$, produced hydrates of stoichiometry $(Ph_4As)RhX_4 \cdot nH_2O$. These diamagnetic complexes ($\chi_g = -0.15 \times 10^{-6}$ cgsu for $(Ph_4As)RhBr_4 \cdot H_2O$) are soluble in solvents such as acetonitrile, dimethylsulfoxide and dimethylformamide and exhibit conductivity behavior in the latter solvent ($\Lambda_m \sim 65$ ohm^{-1} cm^2 mol^{-1} for c ~ 0.3 × 10^{-3}–0.9 × 10^{-3} *M*) which is characteristic of 1:1 electrolytes [8]. Their IR spectra are very similar between 4000 and 500 cm^{-1} and display weak absorption bands at ~3300 and 1640 cm^{-1} which support the presence of water in these complexes. These H_2O absorptions disappear upon the reaction of these salts with acetonitrile which leads to the formation of the adducts $(Ph_4As)RhX_4 \cdot CH_3CN$.

During the preparation of $(Ph_4As)RhCl_4 \cdot 2H_2O$ (following the passage of HCl gas but prior to the addition of Ph_4AsCl), a solid material was filtered off. The X-ray diffraction powder pattern of this residue revealed the presence of Rh(s). This suggests that during the reaction between $Rh_2(O_2CCH_3)_4$ and HX gas in non-aqueous media, disproportionation occurs to give Rh metal and a Rh(III) species. This behavior bears comparison to that reported [9] during studies on Rh_2^{4+}(aq). Rh_2^{4+}(aq) can be formed in solution but its isolation as a simple salt has not been possible [9]. Many anions have been tried as precipitating reagents but it was found [9] that addition of halide anions catalyzes the disproportionation of Rh_2^{4+}(aq) to Rh(s) and Rh(III).

The aquo and acetonitrile adducts $(Ph_4As)RhX_4 \cdot nL$, where X = Cl or Br, L = H_2O or CH_3CN and n = 1 or 2, exhibit well defined X-ray powder diffraction patterns, but in no instance was there evidence for isomorphism between any of the pairs of complexes. The spectral properties of these four complexes (**1–4**) are summarized in Tables I and II. The low frequency

TABLE I. Spectral Properties of Rhodium Halide Complexes.

	Complex	Color	Low frequency IR (400–200 cm^{-1})[a]	Electronic Absorption Spectra (1000–350 nm)	
				Medium[c]	Absorption Maxima (nm)
1	$(Ph_4As)RhCl_4 \cdot 2H_2O$	brown	368m, ~350sh, *~330s,br, 281m*	DR	540, 440
2	$(Ph_4As)RhBr_4 \cdot H_2O$	brown	368m, 353s, *254s, 248s*	NM	570sh, ~470sh, ~380br
3	$(Ph_4As)RhCl_4 \cdot CH_3CN$	pink	368m, *353vs,*[b] *335m-w,* 230w, 215w	DR	495
				CH_3CN	470
4	$(Ph_4As)RhBr_4 \cdot CH_3CN$	pink	369s, 352s, *277s*	DR	530, 380
				CH_3CN	~490sh
5	$RhCl_3(PPh_3)_2(CH_3CN)$	orange	349s, 266w, 248w	NM	450sh
6	$RhBr_3(PPh_3)_2(CH_3CN)$	orange	~231vw	NM	500sh, 380sh
7	$[RhCl_2(dppe)_2]Cl \cdot 2EtOH$[d]	yellow	386m-s, 363s, 338m-s, 306m-w	NM	430sh, 340
8	$[RhBr_2(dppe)_2]Br \cdot 2EtOH$[d]	yellow	~380m-w, br, 282w, ~250w, 227w	DR	460sh?, ~375sh
9	$[RhCl_2(dpae)_2]Cl \cdot 2EtOH$[d]	yellow	399s, 331s, ~320sh, ~280w	NM	450sh; 355
10	$[RhBr_2(dpae)_2]Br \cdot 2EtOH$[d]	yellow	395s, 332s, 312m, 275m	DR	460; 380

[a] ν(Rh–halogen) vibrations are given in italics when these assignments are reasonably certain. [b] This ν(Rh–Cl) mode is coincident with an absorption band of the Ph_4As^+ cation located at ~350 cm^{-1}. [c] DR = diffuse reflectance, NM = Nujol mull. [d] Weak ν(O–H) absorptions (cm^{-1}) due to EtOH are as follows: **7**, 3200; **8**, ~3400; **9**, 3230; **10**, 3350.

IR spectrum of **1**, displays a very close resemblance to that reported by Fergusson and Sherlock [10] for the salt $(Ph_4As)RhCl_4(H_2O)_2 \cdot H_2O$, which contains the *cis*-$[RhCl_4(H_2O)_2]^-$ anion. However, the diffuse reflectance spectra of these two products are quite different (absorptions at 540 and 440 nm for **1** *versus* 483 nm for $(Ph_4As)RhCl_4(H_2O)_2 \cdot H_2O$ [10]) implying that they do not simply differ by the presence of a single molecule of "lattice" water. In view of the lower degree of hydration associated with the bromide complex **2**, it is possible that **1** is best formulated as $(Ph_4As)RhCl_4(H_2O) \cdot H_2O$. The acetonitrile adducts **3** and **4** are of particular interest for two reasons. First, they do not display ν(C≡N) vibrations of any significant intensity in their IR spectra. While this phenomenon is relatively uncommon, it cannot be interpreted to mean that acetonitrile is bound in other than its usual end–on fashion [11, 12], since a crystallographic investigation of the complex $ReCl_3(PPh_3)_2(CH_3CN)$ [13], which also fails to display a ν(C≡N) absorption in its IR spectrum [14], shows the existence of a linear Re–N≡C–CH_3 moiety containing N-bound acetonitrile. The second point or note concerns the presence of only one molecule of acetonitrile in **3** and **4**. This can be contrasted with the formation of the *bis*-nitrile adducts *trans*-$[RhX_4(RCN)_2]^-$, where R = C_6H_5 for X = Cl and R = CH_3 for X = Cl or Br, when Et_4N^+ is used as the counterion [15, 16]. These structural differences are reflected by differences between the low frequency IR and diffuse reflectance electronic absorption spectra of **3** and **4** and those reported [15, 16] for the monomeric $[RhX_4(RCN)_2]^-$ anions. However, since the acetonitrile solution electronic absorption spectra of **3** and **4** (Table I) are in turn different from the related solid-state spectra, the spectrum of **4** resembling in some respects that reported [16] for an acetonitrile solution of $(Et_4N)RhBr_4(CH_3CN)_2$, it is apparent that there is a structure change upon the dissolution of **3** and **4** in this polar, coordinating solvent.

The X-ray photoelectron spectra (XPS) of **1**–**4** (Table II) reveal Rh $3d_{3/2,5/2}$ binding energies which are consistent with the formulation of these complexes as rhodium(III) derivatives [17], while the relatively broad nature of their Cl $2p_{1/2,3/2}$ and Br $3p_{1/2,3/2}$ peaks would support the possibility that they possess structures in which two types of halogen atoms (those in terminal and bridging Rh–X bonds) are present [18, 19]. This would be the case in the halogen-bridged dimers and polymers of the types $[RhX_4L^-]_2$ and $[RhX_4L^-]_n$.

Both the chloride and bromide salts of stoichiometry $(Ph_4As)RhX_4 \cdot nH_2O$, react with triphenylphosphine in refluxing acetonitrile to form the complexes, $RhX_3(PPh_3)_2(CH_3CN)$ (X = Cl or Br), while in ethanol, they react with the bidentate ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,2-bis(diphenylarsino)ethane (dpae) to afford the complexes $[RhX_2(dppe)_2]X \cdot 2EtOH$ and $[RhX_2(dpae)_2]X \cdot 2EtOH$, where X = Cl or Br. These complexes were all characterized by elemental microanalyses and IR and electronic absorption spectroscopy (Table I) and XPS (Table II). A comparison of their properties with those of other analogous rhodium(III) complexes [17, 20], confirmed their

TABLE II. X-Ray Photoelectron Spectra of Rhodium Halide Complexes.[a]

	Complex	Rh		Halogen[b]	
		$3d_{3/2}$	$3d_{5/2}$	$np_{1/2}$	$np_{3/2}$
1	$(Ph_4As)RhCl_4 \cdot 2H_2O$	314.3	309.5(1.5)	199.7	198.4(2.0)
2	$(Ph_4As)RhBr_4 \cdot H_2O$	313.9	309.1(1.7)	188.7	182.1(2.8)
3	$(Ph_4As)RhCl_4 \cdot CH_3CN$	314.5	310.0(1.7)	c	198.3(~1.8)
4	$(Ph_4As)RhBr_4 \cdot CH_3CN$	314.0	309.3(1.4)	188.7	182.0(2.5)
5	$RhCl_3(PPh_3)_2(CH_3CN)$	314.4	309.8(1.5)	199.4	198.1(1.4)
7	$[RhCl_2(dppe)_2]Cl \cdot 2EtOH$	315.0	310.5(1.2)	200.7	199.3(inner sphere Cl)
				198.7	197.1(outer sphere Cl)
8	$[RhBr_2(dppe)_2]Br \cdot 2EtOH$	314.6	309.9(1.2)	189.3	182.3(inner sphere Br)
				188.0	180.9(outer sphere Br)
9	$[RhCl_2(dpae)_2]Cl \cdot 2EtOH$	314.5	309.9(1.1)	200.2	198.6(inner sphere Cl)
				198.4	196.7(outer sphere Cl)
10	$[RhBr_2(dpae)_2]Br \cdot 2EtOH$	314.3	309.7(1)	188.9	182.5(inner sphere Br)
				187.5	181.0(outer sphere Br)

[a] Binding energies referenced to a carbon 1s binding energy of 285.0 eV for the ligands; when appropriate, full-width half-maximum values for certain of the peaks are given in parentheses. [b] 2p for Cl and 3p for Br. In the case of complexes 7–10, the two sets of halogen $np_{1/2,3/2}$ binding energies were obtained by deconvolution procedures (see ref. 22 for full details of the procedure used). [c] Cl $2p_{1/2}$ component poorly defined.

identity. In addition, the dpae derivatives $[RhX_2(dpae)_2]X \cdot 2EtOH$, where X = Cl or Br, were 1:1 electrolytes in nitrobenzene (Λ_m = 20–25 ohm^{-1} cm^2 mol^{-1} for solutions which were 0.5–0.6 $\times$ 10^{-3} *M*).

Like the acetonitrile adducts 3 and 4, the mixed ligand complexes $RhX_3(PPh_3)_2(CH_3CN)$, 5 and 6, fail to exhibit an IR active $\nu(C{\equiv}N)$ mode and their spectra are almost identical to that of the rhenium(III) analog $ReCl_3(PPh_3)_2(CH_3CN)$ [14, 21]. The XPS of 5 (Table II and Figure 1) reveals a well resolved Cl $2p_{1/2,3/2}$ doublet which is characteristic of a single type of chlorine environment.

The electronic absorption spectra of the ionic derivatives **7–10** are in accord with a *trans*-octahedral geometry for the cations. The two absorption maxima between 350 and 470 nm are in excellent agreement with literature data for *trans*-$[RhCl_2(dppe)_2]Cl$ (422 and 347 nm) and the related bis(1,2-dimethylphosphino)ethane (dmpe) complex *trans*-$[RhCl_2(dmpe)_2]Cl$ (408 and 345 sh) [20]. The related *cis*-isomer of $[RhCl_2(dmpe)_2]Cl$ has its lowest energy absorption at 347 nm [20]. The existence of complexes **7–10** as ethanol solvates is in accord with the observations of Butler and Chatt [20] that in contrast to the tendency of *trans*-$[RhX_2(dmpe)_2]X$ to form solvates, the related *cis*-isomers do not do so.

We were unable to interpret the low frequency IR spectra of $[RhX_2(dppe)_2]X \cdot 2EtOH$ and $[RhX_2(dpae)_2]X \cdot 2EtOH$ in terms of a particular stereochemistry for these complexes, a problem similar to that previously encountered [20] in analyzing the related IR spectra of $[RhX_2(dmpe)_2]X$. However, the formulation of complexes **7–10** as ionic species of the type $[MX_2(LL)_2]X$, is confirmed by XPS measurements. All four complexes display halogen $np_{1/2,3/2}$ binding energy spectra (Table II and Figure

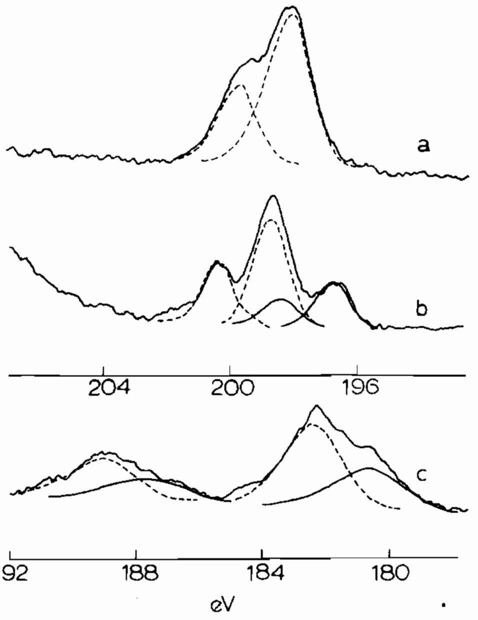

Figure 1. The Cl 2p and Br 3p binding energy spectra of (a) $RhCl_3(PPh_3)_2(CH_3CN)$, (b) $[RhCl_2(dpae)_2]Cl \cdot 2EtOH$ and (c) $[RhBr_2(dpae)_2]Br \cdot 2EtOH$.

1) which possess two sets of overlapping spin-orbit doublets and, therefore, resemble the related Cl $2p_{1/2,3/2}$ spectra of $[RhCl_2L_4]Cl$, where L = pyridine, 1/2(2,2'-bipyridyl) or 1/2(2,5-dithiahexane) [17, 18]. Deconvolution of these spectra, using the procedure we have described previously [22], gave the two sets of halogen $np_{1/2,3/2}$ binding energies listed in Table II. The higher energy doublet has twice the intensity of the lower energy doublet which is assigned to the outer sphere halide anions. The XPS of the bromide complexes **8** and **10** represents the first time that bromine in a terminal M–Br bond (Br_t) has been differentiated from bromide ion (Br^-) by this technique [23]. The energy difference $\Delta E_b(Br_t - Br^-)$ is sufficiently large (~1.4 eV) that it is clear that XPS may be used to advantage in the characterization of metal bromide complexes.

Acknowledgements

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