993. *The Action of Reducing Agents on Pyridine Complexes of Rhodium*(III).

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A series of pyridine complexes originally believed to contain rhodium(II) have been re-studied and shown to be complexes of rhodium(III). Hydridic species have been obtained by reaction of *trans*-dichlorotetrapyridine-rhodium(III) ion with borohydride ion and with hypophosphorous acid.

IN an earlier Paper [1] it was shown that hydridorhodium(III) complexes containing amine ligands are obtained by nucleophilic replacement of the chloride ligand in complex ions such as $[Rhen_2Cl_2]^+$ by using the borohydride ion as a source of hydride ions in aqueous solution. As part of an extension of these and related studies on pyridine complexes of rhodium,[2] certain pyridinerhodium complexes originally believed[3] to contain rhodium(II) were re-investigated. These results are in agreement with, and extend, complementary work carried out on this problem by two of us (B. N. F. and R. S. N.); it is, therefore, convenient to present our results together.

The earlier work [3] was carried out before it was generally recognised that covalent metal–hydrogen bonds could be formed by reduction with various reducing reagents, including hypophosphorous acid.

Although we have obtained evidence for the hydridic nature of certain pyridinerhodium complexes it appears that the most common action of reducing agents on rhodium(III)–pyridine systems is to catalyse, presumably through labile hydridic intermediates, the formation of different rhodium(III) complexes. The behaviour of the chloride and bromides with hypophosphorous acid is as given below; it is clear that most of the apparently rhodium(II) complexes are in fact complexes of rhodium(III), several of which had been characterised earlier by Poulenc,[4] who noted the catalytic effect of alcohol on the formation of rhodium(III) complexes. Similar promotional effects of alcohol have been noted recently in the formation of malonato and diethyldithiocarbamato-complexes of rhodium(III).[5]

Reactions of Pyridine Solutions of Rhodium(III) *Chloride and Bromide with Hypophosphorous Acid.*—It was originally assumed that aqueous solutions of rhodium(III) chloride and bromide heated with an excess of pyridine contained the $[Rh py_6]^{3+}$ ion. Investigations

[1] Gillard and Wilkinson, *J.*, 1963, 3594.
[2] Gillard and Wilkinson, *J.*, 1964, 1224.
[3] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1943, **76**, 275.
[4] Poulenc, *Ann. Chim. (France)*, 1935, **4**, 632.
[5] Klixbull-Jørgensen, Cyanamid European Research Institute report CERI-TIC-P8, 1961, and other references therein.

have shown, however, that such chloride solutions contain 1,2,6-trichlorotrispyridine-rhodium(III) only,[2] and a similar result is now found for the solution of the bromide. In a previous Note [2] it was suggested that the diamagnetic chloro-complex, believed to contain rhodium(II) obtained by the action of hypophosphorous acid on the pyridine complexes in solution, was perhaps a hydride of rhodium(III). We were unable to detect a high-field proton line characteristic of transition-metal–hydrogen bonds in the high-resolution nuclear magnetic resonance spectrum of the yellow solutions and we conclude that the species present is in fact a dichlorotetrapyridinerhodium(III) cation. It appears that the action of the hypophosphorous acid on 1,2,6-trichloropyridinerhodium(III), in the presence of an excess of pyridine, is to catalyse the formation of $[Rh\,py_4Cl_2]^+$ ions; the yellow complex originally believed to be hexakispyridinerhodium(II) chloride [3] is thus identified as the hydrated complex $[Rh\,py_4Cl_2]Cl,5H_2O$ (the rhodium analyses of which do not differ greatly); the corresponding bromo-system is analogous, the product being *trans*-$[Rh\,py_4Br_2]Br$.

The reaction products of these bromo-complexes must also be re-formulated. We have shown that the action of hydrobromic acid on the bromide gives, in fact, the complex *trans*-$[Rh\,py_4Br_2]Br,HBr,2H_2O$ which contains the $[H_5O_2]^+$ ion; [6] continuous washing of this with water removes the excess of acid, leading to *trans*-$[Rh\,py_4Br_2]Br$, believed by Dwyer and Nyholm to have the composition $[Rh\,py_5Br]Br$ which has an almost identical metal content.
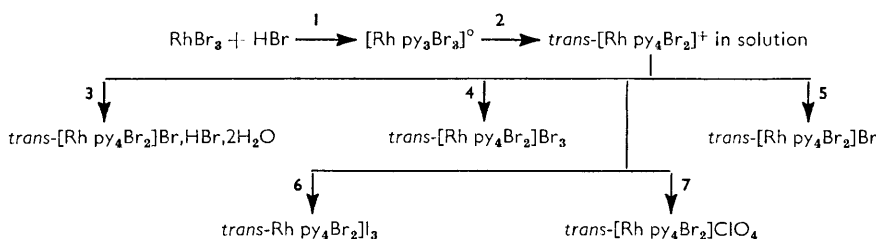
Reagents: 1, Heat with pyridine (excess). 2, Reflux with H_3PO_2 and pyridine. 3, Conc. ice-cold HBr. 4, Bromine water. 5, Aq. NaBr. 6, Aq. KI. 7, NaClO$_4$.

Reactions of rhodium(III)–pyridine complexes.

The earlier [3] conclusions can now be understood, having been based on the assumption that treatment of what was believed to be $[Rh\,py_5Br]Br$ with potassium iodide, etc., simply replaced the anion or, in the case of acids, gradually replaced co-ordinated pyridine. It is now apparent that these replacements of pyridine lead to complexes containing fewer pyridine ligands, as described by Poulenc.[5]

The reactions in the chloro-series are essentially analogous, and a summary of the original and present formulations of the various species is given in the Table. It is note-

Reformation of " rhodous " complexes with pyridine.

Original (ref. 3)	Pesent
$[Rh\,py_6]Br_3$; orange..	1,2,6-Rh py_3Br_3
$[Rh\,py_6]X_2$; yellow	1,6-$[Rh\,py_4Cl_2]Cl,5H_2O$
	1,6-$[Rh\,py_4Br_2]Br$
$[Rh\,py_5X]X$; yellow	1,6-$[Rh\,py_4Cl_2](H_5O_2)Cl_2$
	1,6-$[Rh\,py_4Br_2]Br$
$[Rh\,py_5Br]I$; yellow...	1,6-$[Rh\,py_4Br_2]I$
Rh py_4Br_2; pink-yellow	1,6-$[Rh\,py_4Br_2]1,6$-$[Rh\,py_2Br_4]$
$(pyH)_2[Rh_2py_4Cl_6]$; pink-yellow............................	1,6-$[Rh\,py_4Cl_2]\,1,6$-$[Rh\,py_2Cl_4]$
$(pyH)_4[Rh_2py_2X_8]$; orange-red	$(pyH)1,6$-$[Rh\,py_2X_4]$ (X = Cl or Br)

worthy that the original analyses for rhodium [3] agree well with both the original and revised formulations since the molecular weight of pyridine and the atomic weight of bromine are approximately equal. However, bromine analyses in the presence of rhodium are unreliable when standard methods are used and long refluxing with silver nitrate

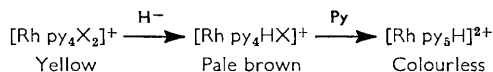[6] Gillard and Wilkinson, *J.*, 1964, 1640.

solution is often needed to remove co-ordinated halogen from rhodium(III) complexes. The compounds listed in the Table show no reducing properties, except that those compounds containing $[Rh py_4X_2]^+$ very slowly interact with alcoholic silver nitrate as observed,[3] but this is attributable to the formation of transitory hydridic species by the action of alcohol which can then reduce the silver ion.

The complex $[Rh py_4Br_2]Br$ does not reduce silver nitrate in acetone solution, showing the importance of alcohol in the reduction. Treatment with sodium perchlorate yields the compound $[Rh py_4Br_2]ClO_4$ which was obtained analytically pure. Both $[Rh py_4Br_2]Br$ and the perchlorate have molecular conductivities in nitrobenzene and water ($\sim$25 and 100 mhos, respectively) which are indicative of 1 : 1 electrolytes.

The compound $[Rh py_4Br_2]Br$ reacts readily with halogens, to form complexes in which the polyhalide anions of the type Br_3^-, I_3^-, etc., are present. Prolonged treatment of the compound $[Rh py_4Br_2]Br_3$ with sodium perchlorate in hot water yields the simple perchlorate.

Certain other complexes described originally,[3] which were difficult to characterise, now appear to be mixtures. The fully halogenated final products are either pyridinium salts of the $[RhHal_6]^{3-}$ ion or of the $[Rh_2(Hal)_{10}]^{4-}$ ion.

Hydridorhodium Complexes.—The reactions of cold aqueous solutions of *trans*-dichlorotetrapyridinerhodium cation and its bromo-analogue with borohydride ion and with hypophosphorous acid lead to hydridic complexes. The yellow solutions of the dihalogeno-complexes first become brown, and a high-field proton resonance line at τ *ca.* 28·5 is observed in all four cases. Crystals can be obtained from the solutions of the bromo-compound and these show a strong infrared band at *ca.* 2000 cm.$^{-1}$ attributable to the Rh–H stretching mode. The brown solutions do not appear to react further, even with an excess of borohydride ion; but, when an excess of pyridine is present with either borohydride or hypophosphorous acid, the brown solutions become colourless on boiling, as observed earlier,[3] and these colourless solutions again show high-field proton resonances at τ *ca.* 29; we have been unable to isolate solids from these solutions of the chloro- and bromo-complexes. However, the iodide affords very pale yellow, extremely air-sensitive crystals of what was originally[3] believed to be " hexakispyridinerhodium iodide." These have a strong band at 1980 and a band at 822 cm.$^{-1}$, presumably due to the Rh–H stretch and bend, respectively. A tentative explanation of these results is:

$$[Rh\ py_4X_2]^+ \xrightarrow{\ H^-\ } [Rh\ py_4HX]^+ \xrightarrow{\ Py\ } [Rh\ py_5H]^{2+}$$
$$\quad\ \ \text{Yellow} \qquad\qquad\ \text{Pale brown} \qquad\qquad\ \text{Colourless}$$

Support for the formation of the brown species as tetrapyridine complexes is given by the observations that the yellow salt $[Rh py_4Br_2]Br$ was obtained from a brown solution containing an excess of bromide ion and also that the reaction of the brown solutions with carbon tetrachloride gives the $[Rh py_4Cl_2]^+$ ion. Analytical results are in only fair agreement with the above scheme and the extreme instability and air-sensitivity of the solids precludes any accuracy. For $[Rh py_4Cl_2]^+$ the lowest-energy *d–d* band at 410 mμ disappears on formation of the brown solution, and an intense broad featureless absorption rising into the ultraviolet prevents observation of any *d–d* bands for the hydridic ion.

Isolation of rhodium complexes containing co-ordinated iodine is very difficult; the only compound we have been able to isolate other than the above unstable hydride is brown tri-iodotripyridinerhodium(III), which is formed by decomposition of the initial product of the reaction of rhodium(III) iodide with pyridine in the presence of hypophosphorous acid. This initial product forms brown-yellow crystals and is probably *trans*-di-iodotetrapyridinerhodium(III) iodide, but attempting to dry it or to wash it with water, alcohol, or ether causes ready loss of pyridine and a material $Rh py_3I_3$ remains as a water-insoluble residue. The initial product is stable only in presence of an excess of pyridine.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Nuclear magnetic resonance spectra were obtained by using a Varian Associates V4311 spectrometer at 56·43 Mc./sec. with large insert for tubes of 15-mm. outside diameter. Infrared spectra were taken on a Grubb–Parsons Spectromaster (Nujol mulls were prepared in an inert-atmosphere box) and electronic spectra on a Perkin-Elmer model 4000 spectrophotometer.

The preparations were carried out under nitrogen, and solvents were thoroughly deoxygenated before use; operations were carried out under nitrogen where necessary. It is convenient to summarise the corrected formulations with analytical data concerning the various complexes.

trans-*Dibromotetrapyridinerhodium*(III) *Bromide.*—This was originally believed to be [Rh py$_5$Br$_2$]. It was obtained as yellow prisms, soluble in ethanol, in agreement with the original description.[3] The infrared and electronic spectra of this *product* were in complete agreement with those of an authentic sample of 1,6-dibromotetrapyridinerhodium(III) bromide, which in turn agreed with recorded values [7] (Found: C, 36·2; H, 3·1; N, 8·4. C$_{20}$H$_{20}$Br$_3$N$_4$Rh requires C, 36·45; H, 3·1; N, 8·5%).

trans-*Dibromotetrapyridinerhodium*(III) *Perchlorate.*—This was prepared in order to confirm the cation by adding sodium perchlorate solution to a solution of the corresponding monobromide; this *salt* is obtained as an anhydrous pale yellow powder (Found: C, 35·7; H, 2·9; Br, 22·9; Rh, 15·3. C$_{20}$H$_{20}$Br$_2$ClN$_4$O$_4$Rh requires C, 35·4; H, 3·0; Br, 23·6; Rh, 15·2%). The complex is a 1 : 1 electrolyte (27·2 mhos) at 0·001M in nitrobenzene.

trans-*Dibromotetrapyridinerhodium*(III) *Bromide*, 2H$_2$O,HBr.—This *salt* was prepared by treating an ice-cold solution of the monobromide with concentrated hydrobromic acid. The golden-yellow plates [3] first obtained have the composition 1,6-[Rh py$_4$Br$_2$][H$_5$O$_2$]Br$_2$, analogous to the chloride, 1,6-[Rh py$_4$Cl$_2$](H$_5$O$_2$)Cl$_2$,[4] as shown by the similarity in infrared spectra. Bands occur at 2900vb,s, 2200b, 1660b,m, 1601m, 1480w, 1207m, 1150m, 1060m, 1017m, 940vb, 771sh, 762, and 693s cm.$^{-1}$. Since washing removes the added HBr,2H$_2$O, the material analysed [3] apparently had the composition [Rh py$_4$Br$_2$]Br (Found: [3] Rh, 15·6. C$_{20}$H$_{20}$Br$_3$N$_4$Rh requires Rh, 15·6%).

trans-*Dibromotetrapyridinerhodium*(III) *Iodide.*—The *iodide* originally believed to have a structure [Rh py$_5$Br]I. It was prepared by treating an aqueous solution of the above monobromide with potassium iodide solution (Found: [3] Rh, 14·9. C$_{20}$H$_{20}$Br$_2$IN$_4$Rh requires Rh, 14·6%), identical with an authentic sample.[8]

1,2,6-*Tribromotripyridinerhodium*(III).—As has been described,[3] when the salt [Rh py$_4$Br$_2$]Br is refluxed with 2N-hydrobromic acid containing a few drops of hypophosphorous acid, a yellow solution is gradually formed. In one experiment this solution was cooled and diluted with water, whereupon 1,2,6-tribromotripyridinerhodium(III) separated (Found: C, 30·9; H, 2·8; Br, 40·75; N, 7·5. C$_{15}$H$_{15}$Br$_3$N$_3$Rh requires C, 31·1; H, 2·6; Br, 41·35; N, 7·25%), $\lambda_{max.}$ in acetone, 458 mμ (ε 182) (lit.,[7] 460 mμ, ε 186). Other bands and the infrared spectrum agreed with published data.[7] However, 1,2,6-tribromotrispyridinerhodium(III) is apparently not compound (V) of ref. 3 but an intermediate, since on prolonged refluxing of the yellow solution a buff precipitate is formed. This substance, of properties identical with those of compound (V), is [Rh py$_4$Br$_2$][Rh py$_2$Br$_4$],[4] which is isomeric with Rh py$_3$Br$_3$ (Found: C, 31·2; H, 2·8; N, 7·2; Rh,[3] 17·8. Calc. for C$_{30}$H$_{30}$Br$_6$N$_6$Rh$_2$ as above and Rh, 17·7%) and has $\nu_{max.}$ 1606m, 1480w, 1240w, 1218m, 1150m, 1070s, 1020m, 774s, 766m, 754m, 699s, 695sh, and 693sh cm.$^{-1}$, agreeing with an authentic sample within 1 cm.$^{-1}$.

Pyridinium Tetrabromobispyridinerhodate(III).—It is now clear that this compound [4] is formed after prolonged treatment with hydrobromic acid. The analyses agree well with those found [3] originally for what was believed to be [pyH]$_4$[Br$_3$py RhBr$_2$Rh pyBr$_3$].

Chloro-complexes.—We have now shown that the pale yellow crystals originally believed to have the composition [Rh py$_6$]Cl$_2$ are in fact those of the hydrate [Rh py$_4$Cl$_2$]Cl,5H$_2$O; similarly the complex originally believed to be [Rhpy$_5$Cl]Cl is re-formulated as *trans*-[Rh py$_4$Cl$_2$]Cl,HCl,2H$_2$O which loses hydrogen chloride when washed. As a result the analysis is indefinite and depends upon time of washings.

The complex believed to have the structure [pyH]$_2$[Cl$_2$py$_2$RhCl$_2$Rh py$_2$Cl$_2$] is in fact the salt 1,6-[Rh py$_4$Cl$_2$]1,6-[Rh py$_2$Cl$_4$] described by Delépine [9] and obtained by a similar procedure

[7] Schmidtke, Cyanamid European Research Institute report CERI-TIC-P25, 1962.
[8] Jørgensen, *J. prakt. Chem.*, 1890, **41**, 440.
[9] Delépine, *Bull. Soc. chim. France*, 1929, **45**, 235.

(Found: C, 40·6; H, 3·7; N, 9·8. Calc. for $C_{30}H_{30}Cl_6N_6Rh_2$: C, 40·3; H, 3·4; N, 9·4%). The electronic (reflectance) and infrared spectra agreed with those [2] of an authentic sample.

Finally the compound originally formulated as $[pyH]_4[Cl_3py_2RhCl_2Rh\ py_2Cl_3]$ is now found to be identical with $[pyH][Rh\ py_2Cl_4]$ as reported by Delépine.[9] The electronic and infrared spectra agree with those previously reported.

" *Hexakispyridinerhodium*(II) *Iodide.*"—Using the original procedure [3] we obtained the extremely unstable air-sensitive pale yellow crystals. Analyses are not satisfactory but we tentatively formulate the compound as hydridopentapyridinerhodium(III) iodide (originally believed to be $[Rh\ py_6]I$) (Found: I, 31·2; [3] Rh, 12·6.[3] Calc. for $C_{25}H_{26}I_2N_5Rh$: I, 33·7; Rh, 13·7%). The infrared spectrum showed bands at 1990s, 1601m, 1590m, 1490w, 1478w, 1239w, 1221m, 1160s, 1155sh, 1068s, 1047w, 1039m, 1020m, 997m, 987w, 960w, 941w, 822m, 779s, 769s, 749s, 702sh, 698s cm.$^{-1}$.

Tri-iodotrispyridinerhodium(III).—Rhodium trichloride solution (10 ml. containing 0·09 g. of rhodium) was treated with potassium iodide (3 g. in 3 ml. of water). When the mixture was heated, the dark iodorhodate(III) ion was formed and at this stage pyridine (12 ml.) and 30% hypophosphorous acid (2 ml.) were added. The mixture was warmed until the colour faded to brown, then rapidly cooled, whereupon *trans*-di-iodotetrapyridinerhodium(III) iodide began to crystallise. This yellow-brown compound was collected (a sample dried on a porous tile showed infrared bands at 1610s, 1544m, 1482w, 1242m, 1220m, 1165s, 1082m, 1069m, 1048s, 1021m, 998w, 960w, 765s, 749m, and 702s cm.$^{-1}$) and washed copiously with water; during washing, the colour changed to red-brown. When the washings no longer contained pyridine the red-brown residue of the *compound* was air-dried and crystallised from dichloromethane (yield, 0·2 g.) (Found: I, 52·5; N, 6·1. $C_{15}H_{15}I_3N_3Rh$ requires I, 52·8; N, 5·8%).

Action of Halogens on trans-*Dibromotetrapyridinerhodium*(III) *Bromide.*—The salt *trans*-$[Rh\ py_4Br_2]Br$ in aqueous solution reacts instantly with bromine and with iodine in potassium iodide solution to produce precipitates which have the general formula $[Rh\ py_4Br_2]X_3$ (X = Br or I). For the yellow tribromide (Found: C, 29·8; H, 2·15; Br, 48·2; N, 6·9; Rh, 12·5. Calc. for $C_{20}H_{20}Br_5N_4Rh$: C, 29·3; H, 2·5; Br, 48·8; N, 6·8; Rh, 12·6%). This substance is a 1 : 1 electrolyte in 0·001M-solution in nitrobenzene (29·6 mhos) or acetone (164 mhos). The yellow-brown triodide (Found: C, 25·8; H, 2·2; N, 5·9; Rh, 10·4. Calc. for $C_{20}H_{20}Br_2I_3N_4Rh$: C, 25·0; H, 2·1; N, 5·8; Rh, 10·7%) is also a 1 : 1 electrolyte (molecular conductivity in 0·001M-solution 27·5 mhos in nitrobenzene and in acetone 140 mhos).

Reaction of trans-*Dibromotetrapyridinerhodium*(III) *Bromide with Reducing Agents.*—*trans*-$[Rh\ py_4Br_2]Br$ (0·66 g., 10^{-3} mole) in water (5 ml.) was treated with hypophosphorous acid (0·2 ml.) and heated to boiling, whereupon the yellow solution became brown. The solution was cooled rapidly in an inert atmosphere and set aside in an ice-bath. After 6 hr., the brown acicular crystals (0·2 g.) which had appeared were collected in an inert atmosphere. Analytical results were inconclusive, because of the instability of the compound; formulation as a hydride is based on the observation of a high-field line in the brown solution (τ 28·5) and the infrared spectrum, which shows bands at 1976s, 1605m, 1592s, 1487w, 1479w, 1238m, 1223m, 1159s, 1154m, 1067m, 1021m, 996m, 942w, 781s, 768s, 747s, 703m, and 698 cm.$^{-1}$.

A brown solution showing a high-field line (τ 28·5) was also obtained by treating an aqueous (or alcoholic) solution of the salt $[Rh\ py_4Br_2]Br$ with aqueous sodium borohydride, but in this case no crystals were obtained. Similar experiments on the dichloro-species, *trans*-$[Rh\ py_4Cl_2]Cl$, gave pale brown solutions (showing high-field lines, τ 28·5) with hypophosphorous acid or borohydride ion, but no crystals were obtained in these cases. In the presence of an excess of pyridine, the brown solutions became colourless on boiling and showed high-field lines at τ 29. The electronic spectrum of the chloride *trans*-$[Rh\ py_4Cl_2]Cl$ shows a band at 408 mμ with $\varepsilon = 75$. After treatment with borohydride, a broad featureless absorption rising into the ultraviolet region was found for the brown solution; the extinction coefficient per g.-atom of rhodium at 408 mμ was then 2×10^3.