A Study of the Co-ordination Behaviour of Various 2-Pyridylketones. Part II.¹ Rhodium(III) Complexes of 2-Benzoylpyridine

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Reaction of rhodium trichloride and 2-benzoylpyridine (PhCOpy) in ethanol affords the complex $Rh(PhCOpy)_2Cl_2,Rh(PhCOpy)Cl_4$. The cation has been obtained as perchlorate in yellow and orange isomeric forms. Both isomers have *trans* chloride ligands. Reaction of any of these compounds with bolling water gives $Rh(PhCOpy)_2Cl_2,OH$, a neutral six-co-ordinate rhodium(III) complex containing one unidentate 2-benzoyl-pyridine molecule co-ordinated *via* oxygen. Reflexing the last compound in aqueous ethanol gives a further neutral complex, $Rh(PhCOpy)_2Cl_3$ containing one molecule of benzoylpyridine co-ordinated through nitrogen only Another neutral complex [$Rh(PhCOpy)_2Cl_3,H_2O$]. H_2O]: H_2O]:

Corresponding bromo-complexes have been prepared and spectroscopic data, including assignments of rhodium-halogen stretching frequencies, are presented.

Few complexes of rhodium(III) with unsymmetrical chelate ligands are known. This and other reasons led to this study.

Physical data for some new solid rhodium(III) complexes are in the Table 1. The Scheme illustrates some possible reactions and interconversions of the new compounds. differs from that of the orange dimethylformamide solution. If complex 2 is gently warmed with water it is converted into an orange isomer No. 3. Only one dibromo-complex (No. 5) was obtained as perchlorate. The single rhodium-chlorine stretching frequency observed for compounds 2 and 3 suggests both compounds to be *trans*-dichloro-complexes. Also compound 2

Solid-state spectral data for complexes of rhodium(III) with 2-benzoylpyridine

			Diffuse reflectance	I.r. spectra		
No.	Complex	Colour	spectrum (kk)	ν (C=O)	$\nu(OH/OD)$	$\nu(RhX)$
1	$Rh(PhCOpy)_{2}Cl_{2}, Rh(PhCOpy)Cl_{4}$	Orange	22.7sh, 20.6	1510 - 1520		372
				1545		341, 330sh, 326
1a	Ph ₄ As•Rh(PhCOpy)Cl ₄	Orange	22.7			347, 336b
2	$Rh(PhCOpy)_2Cl_2,ClO_4$	Yellow	23.8, 21.5	1520 - 1530		377
3	Rh(PhCOpy) ₂ Cl ₂ ,ClO ₄	Orange	23·5, 21·5sh, 18·2sh	1515 - 1530		373
4	$Rh(PhCOpy)_{2}Br_{2}, Rh(PhCOpy)Br_{4} \dots$	Orange-red	22.6, 20.8sh	1515 - 1522		273
				1547		234b
5	$Rh(PhCOpy)_{2}Br_{2},ClO_{4}$	Pale orange	$25 \cdot 0 sh$	1520 - 1527		
6	Rh(PhCOpy) ₂ Cl ₂ (OH)	Red	22.2, 19.1	1554	3395	349
6a	$Rh(PhCOpy)_2Cl_2(OD)$	Red		1555	2520	348
7	$Rh(PhCOpy)_2Br_2(OH)$	Red	22·5, 19·4	1554	3410	263
0	Ph(PhCOpy) Cl	Vallour	95.0 91.5-h	∫ 1669		365
0	$\operatorname{Kir}(1\operatorname{ICOpy}_2 \odot I_3 \ldots \ldots$	1 CHOW	20.0, 21.0511	1565		342, 314
0	Rh/Ph(Opy) Br	Vallow	No maxima < 20.0	∫ 1668		275, 261, 234
3	$\operatorname{Kn}(1\operatorname{ncopy})_2\operatorname{Di}_3$	1 CHOW	10 maxima < 50.0	1565		
10	Rh(PhCOpy)Cl ₃ ,2H ₂ O	Orange	22.7	1534 - 1537	3520 - 3440	354, 328 *
11	Rh(PhCOpy)Br ₃ ,2H ₂ O	Deep orange	No maxima resolved	1530 - 1540	3500b	269,* 232
		- •	~ 30.0			

* Mixed with ligand modes.

The reaction of commercial rhodium(III) chloride trihydrate with 2-benzoylpyridine in ethanolic media gives dichlorobis-(2-benzoylpyridine)rhodium(III) tetrachloro-(2-benzoylpyridine)rhodate(III) (No. 1, Table); the corresponding bromo-complex (No. 4) has been prepared. Analytical and conductivity data are consistent with the given formulations; also it is possible to prepare the yellow complex (No. 2) *trans*-dichlorobis-(2-benzoylpyridine)rhodium(III) perchlorate by the metathesis of compound 1 with sodium perchlorate. A specimen of the complex rhodate(III) has been obtained as the tetraphenylarsonium salt (No. 1*a*).

Complex 2 is a uni-univalent electrolyte in both nitromethane and dimethylformamide solutions; however the spectrum of the yellow nitromethane solution forms an adduct $Rh(PhCOpy)_2Cl_2,HCl,2H_2O$ which has been taken to indicate a *trans* complex.²

Thin-layer chromatography has shown nitromethane solutions of complexes 2 and 3 to contain mainly complex 2 whereas the dimethylformamide solutions contain principally compound 3. We assign the structure *trans*-dichloro-*trans*-bis-(2-benzoylpyridine)rhodium(III) perchlorate to compound 2 and consider compound 3 to contain *trans*-chloride ligands and *cis*-2-pyridyl groups. The richer visible spectrum supports the lower microsymmetry envisaged for compound No. 3.

When compounds 3 and 5 are treated with boiling water deep red materials of composition $Rh(PhCOpy)_2X_2OH$ (X = Cl, No. 6; X = Br, No. 7) are produced. Both complexes are non-electrolytes, but

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¹ Part I, R. R. Osborne and W. R. McWhinnie, J. Chem. Soc. (A), 1967, 2075.

dimethylformamide solutions of No. 6 show some degree of non ionic dissociation. The i.r. spectra of compounds 6 and 7 are more complex than those of compounds previously considered, particularly in regions associated with the 2-pyridyl group. The presence of the hydroxo-groups has been confirmed by deuteriation

conc. (a) - $Rh(PhCO py)_2Cl_2$, $Rh(PhCO py)Cl_4$ (a) $Rh(PhCO_{Py})_{2}Cl_{2},Cl_{2}HCl_{2}H_{2}O \leftarrow Rh(PhCO_{Py})_{2}Cl_{2},ClO_{4}$ (yellow) CI (b) (4) $Rh(PhCO_{py})_{2}(py)Cl_{2},ClO_{4}$ Rh(PhCO py)2Cl2,ClO4 (orange) excess (b) (c) Rh(py)₄Cl₂,ClO₄ ĊI (e) Rh(PhCO py), Cl, OH (g) Rh(PhCO py)2CI3

 $Rh(PhCO_{Py})Cl_{3}H_{2}O,H_{2}O$

Scheme Reactions of 2-benzoylpyridine complexes of rhodium(III) chloride

Reagents: (a) HCl, (b) pyridine, (c) $HClO_4$, (d) H_2O /reflux, (e) filter, (f) EtOH, (g) filtrate left to stand.

studies and the single rhodium-halogen stretching frequency implies *trans*-halogeno-ligands, and the lower frequency of this vibrational mode for complex 6 than for complex 2 is consistent with the change from a neutral to a cationic complex. Compounds 6 and 7 are therefore considered to be a hydroxo-*trans*-dihalogenobis-(2-benzoylpyridine)rhodium(III) containing one unidentate (*via* oxygen) and one bidentate 2-benzoylpyridine molecule.

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The two hydroxo-compounds may also be prepared from compounds 1 and 4. When the filtrates from these preparations are allowed to stand, well-formed orange crystals of the neutral complexes $[Rh(PhCOpy)X_3,H_2O]H_2O$ (X = Cl, Br; Nos. 10 and 11) are deposited. We consider these compounds to arise from the slow aquation of the tetrachloro-(2-benizoylpyridine)rhodate(III) anion.

Treatment of the hydroxo-complexes 6 and 7 with refluxing ethanol, or of compounds 1 and 4 with sodium chloride and lithium bromide respectively, affords the complexes bright yellow chloroform soluble Rh(PhCOpy)₂Cl₃ (No. 8) and Rh(PhCOpy)₂Br₃ (No. 9). Both are non-electrolytes (although No. 8 undergoes considerable non ionic dissociation in dimethylformamide) and both give i.r. spectra which contain bands associated with free and with co-ordinated carbonyl We consider the compounds to be transgroups. trihalogenobis-(2-benzoylpyridine)rhodium(III) and note that this formulation is supported by the presence of three rhodium-halogen stretching modes of sensible intensity (this pre-supposes that it is sufficient to consider the local symmetry of the RhCl₃ unit). The compounds contain one molecule of benzoylpyridine coordinated via nitrogen only. These complexes are similar to those of rhodium(III) with o-methoxyphenyldimethylarsine and with o-dimethylaminophenyl dimethylarsine recently reported by Panattoni et al.³

Finally the reaction of compound 2 with excess of pyridine gives *trans*-dichlorotetrapyridinerhodium(III) perchlorate in good yield *via* an ill-defined complex of stoicheiometry Rh(PhCOpy)₂(py)Cl₂,ClO₄.

EXPERIMENTAL

Diffuse reflectance spectra (against magnesium carbonate) and solution spectra were measured with Unicam SP 500 and SP 700 instruments respectively. I.r. spectra were determined for Nujol and hexachlorobutadiene mulls with a Perkin-Elmer 237 grating instrument, far-i.r. spectra were measured with Grubb-Parsons DM4 (667—222 cm.⁻¹) and Perkin-Elmer 225 (400—200 cm.⁻¹) spectrophotometers. Conductivity measurements were obtained with a Doran bridge.

trans-Dichlorobis(2-benzoylpyridine)rhodium(III) Tetrachloro-(2-benzoylpyridine)rhodate(III).—Ethanolic solutions (5 ml.) of rhodium trichloride trihydrate (0.26 g.) and 2-benzoylpyridine (0.37 g.) were mixed. The resulting solution was heated under reflux for 30 min. The orange solid which deposited on cooling was washed with ethanol (yield 0.41 g.). This, together with other compounds described, was vacuum-desiccated over P_4O_{10} (Found: C, 44.6; H, 2.8; Rh, 20.7. $C_{36}H_{27}Cl_6N_3O_3Rh_2$ requires C, 44.7; H, 2.7; Rh, 21.3%); Λ_M (10⁻³M in dimethylformamide) 62.

trans-Dichlorobis-(2-benzoylpyridine)rhodium(III) Perchlorate.—(Yellow isomer). To a solution of rhodium trichloride trihydrate (0.26 g.) in ethanol (10 ml.) was added an aqueous ethanolic (5 ml.; 50% v/v) solution of 2-benzoyl-

 ² R. D. Gillard and G. Wilkinson, J. Chem. Soc., 1964, 1640.
³ C. Panattoni, L. Volponi, G. Bombieri, and R. Graziani, Gazzetta, 1966, 96, 1158; 1967, 97, 1006; Chem. Comm., 1967, 977, 1284. pyridine (0.37 g.) and sodium perchlorate (1.23 g.). The resulting solution was heated under reflux for 30 min. The yellow *product* was washed with cold water and ethanol (yield 0.45 g.). The same complex was obtained from the metathesis of compound No. 1 (Table) and sodium perchlorate in aqueous ethanol (Found: C, 45.0; H, 2.9; N, 4.55; Rh, 16.0. C₂₄H₁₈Cl₃N₂O₆Rh requires C, 45.0; H, 2.8; N, 4.4; Rh, 16.1%).

Orange isomer. The above complex (0.2 g.) was warmed for several minutes with distilled water. The orange product was washed with cold water (yield 0.19 g.) (Found: C, 45.4; H, 3.6; Rh, 16.3). Solutions of either isomer are yellow in nitromethane and orange in dimethylformamide. Each solution was shown to contain two components by t.l.c. on Kieselguhr G with dimethyl ether-dichloromethane (1:1) for elution [Λ_M 71 (No. 2), 75 (No. 3) (10⁻³M in dimethylformamide); Λ_M 88 (No. 2), 94 (No. 3) (10⁻³M in MeNO₂)].

trans-Dibromobis-(2-benzoylpyridine)rhodium(III) Tetrachloro-(2-benzoylpyridine)rhodate(III).—Dry lithium bromide (1·3 g.) and 2-benzoylpyridine (0·54 g.) were dissolved in ethanol (20 ml.) and added to an ethanolic solution (10 ml.) of rhodium trichloride trihydrate (0·39 g.). The solution was heated under reflux for 30 min. The dark orange solid was filtered off and washed with ethanol (yield 0·8 g.) (Found C, $35\cdot2$; H, $2\cdot2$; N, $3\cdot5$; Rh, $16\cdot6$. C₃₆H₂₇Br₆N₃O₃Rh₂ rerequires C, $35\cdot0$; H, $2\cdot2$; N, $3\cdot4$; Rh, $16\cdot7\%$); AM (10^{-3} M in dimethylformamide) 42.

trans-Dibromobis-(2-benzoylpyridine)rhodium(III) Perchlorate.—A suspension of the above complex (0.2 g.) in saturated aqueous sodium perchlorate was allowed to stand for a few minutes. The pale orange solid was filtered off and washed with water (yield 0.12 g.) (Found: C, 39.7; H, 2.4; N, 3.9; Rh, 14.0. $C_{24}H_{18}Br_2CIN_2O_8Rh$ requires C, 39.5; H, 2.5; N, 3.8; Rh 14.1%); Λ_M (10⁻³M in dimethylformamide) 69, (10⁻³M in MeNO₂) 93.

trans-Dichloro-(or Dibromo) hydroxobis-(2-benzoyl pyridine)rhodium(III).—Complex No. 1 (Table) (0.3 g.) was refluxed in distilled water (15 ml.) for 15 min. The red solid formed was filtered off and washed with water. The same product was obtained from a similar treatment of complexes 2 and 3. The bromide was obtained from complex 4 or 5. Substitution of deuterium oxide for water gave the deuteriated product [Found: C, 51.9; H, 3.5; Rh, 18.4%; M (Mechrolab osmometer, 0.04M in dimethylformamide 350. $C_{24}H_{19}Cl_2N_2O_3Rh$ requires C, 51.7; H, 3.8; Rh, 18.5; M, 557] (Found: C, 44.7; H, 3.1; Rh, 15.9. $C_{24}H_{19}Br_2N_2O_3Rh$ requires C, 44.6; H, 3.0; Rh 16.0%); Λ_M (10⁻³M-chlorocomplex in dimethylformamide) 7.1, (10⁻³M-bromo-complex in dimethylformamide) 17.

trans-Trichloro-(and Bromo-)bis-(2-benzoylpyridine)rhodium(III).—Dichloro-(or dibromo-)hydroxobis-(2-benzoylpyridine)rhodium(III) (0·39 g.) was refluxed with 75% aqueous ethanol (10 ml.) for 3 hr. The yellow product was recrystallised from chloroform [Found: C, 49·5; H, 3·8; N, 4·6%; *M* (Mechrolab, osmometer) 452 (0·04M in dimethylformamide), 345 (0·06M in dimethylformamide). C₂₄H₁₈Cl₃N₂O₂Rh requires C, 50·0; H, 3·2; N, 4·9%; *M*, 576] (Found: C, 40·9; H, 2·7; N, 4·0; Rh, 14·7. C₂₄H₁₈Br₃N₂O₂Rh requires C, 40·7; H, 2·5; N, 4·0; Rh, 14·6%); $\Lambda_{\rm M}$ (10⁻³M-chloro-complex in dimethylformamide) 4.

Reaction of Rh(PhCOpy)₂X₂,Rh(PhCOpy)X₄ (X = Cl, Br) with Water.—The initial reaction of complexes 1 or 4 with boiling water gives a precipitate of complexes 6 or 7. If the filtrate is allowed to stand for several days after removal of the insoluble hydroxo-complex, crystals of an orange material Rh(PhCOpy)X₃,2H₂O (X = Cl, Br) are formed (Found: C, 34·3; H, 3·1; N, 3·4; Rh, 23·6. C₁₂H₁₃Cl₃NO₃Rh requires C, 33·6; H, 3·0; N, 3·3; Rh, 24·0%) (Found: C, 26·4; H, 2·7; N, 3·0. C₁₂H₁₃Br₃NO₃Rh requires C, 29·9; H, 2·7; N, 2·9%); $\Lambda_{\rm M}$ (10⁻³M-chlorocomplex in dimethylformamide 2·5, (10⁻³M-bromo-complex in dimethylformamide) 7·2.

Tetraphenylarsonium Tetrachloro-(2-benzoylpyridine)rhodate(111).—Tetraphenylarsonium chloride (0.63 g., 1.5 mmoles) and rhodium trichloride trihydrate (0.12 g., 0.5 mmoles) were dissolved in ethanol (20 ml.). 2-Benzoylpyridine (0.09 g., 0.5 mmoles) in ethanol (5 ml.) was added and the combined solution was refluxed for 30 min. The orange product was filtered off (yield 0.25 g.) (Found: N, 1.5. $C_{36}H_{29}AsCl_4NORh$ requires N, 1.7%); Λ_M (10⁻³M in MeNO₂) 71.

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