A STUDY OF THE CO-ORDINATION BEHAVIOUR OF 2-PYRIDYLKETONES PART III*. ACETYL- AND SUBSTITUTED BENZOYL-2-PYRIDYL COMPLEXES OF RHODIUM(III)

ROSEMARY R. OSBORNE AND W. R. MCWHINNIE

Department of Chemistry, The University of Aston in Birmingham, Birmingham (Gt. Britain) (Received September 7th, 1968)

SUMMARY

The electronic effect of the group R* in the ligands PyCOR (R=Me, 2-py, 2-(m-C₆H₄·NH₂), 2-(m-C₆H₄·NO₂)) on the following substitution reaction is considered: trans-[Rh(pyCOR)Cl₂]⁺ \rightarrow [Rh(pyCOR)(pyCOR-unidentate)Cl₂·OH].

The preparations and characterisation of several new complexes of rhodium(III) with ketonic ligands are also reported.

INTRODUCTION

We recently reported the preparation of a new series of rhodium(III) complexes with 2-benzoylpyridine¹ and in particular noted an unusual substitution reaction of the *trans*-dichlorobis-(2-benzoylpyridine)rhodium(III) cation involving the rupture of a chelate ring to give a product containing a unidentate 2-benzoylpyridine molecule bonded to rhodium(III) through the carbonyl oxygen atom. The reaction proceeded *via* an isomeric form of $[Rh(pyCOPh)_2Cl_2]^+$:



In this paper we attempt to consider the generality of this reaction by (a) attempting to introduce other nucleophiles and (b) by considering complexes of other 2-pyridyl-ketones.

R = Me, 2-pyridyl-, *m*-nitrophenyl-, *m*-aminophenyl-* Part II, see ref. 1.

J. Less-Common Metals, 17 (1969) 53-57

EXPERIMENTAL

2-Acetylpyridine and di-2-pyridylketone were available commercially. 2-(*m*-Nitrobenzoyl)pyridine was prepared by the method of HANDS AND KATRITZKY³. The ligand was recrystallised from ethanol to m.p. $116^{\circ}-117^{\circ}$ C (lit. 117° C³).

2-(m-Aminobenzoyl)pyridine. This is a new compound. The method of SCHOFIELD⁴ for the reduction of 2-(p-nitrobenzoyl)pyridine was used. 2-(m-Nitrobenzoyl)pyridine (5 g) in conc. hydrochloric acid (5 ml) was treated with a solution of stannous chloride (15 g) in conc. hydrochloric acid (20 ml) during 5 min; the solution was then heated for 1 h at 95°C and then set aside for 5 h at room temperature. The mixture was made alkaline with conc. NaOH and extracted with ether. Removal of solvent gave a dark oil which could not be crystallised, yield 1.5 g. It was shown to be a single compound by TLC (ν (CO), 1630 cm⁻¹; δ (NH₂), 1660 cm⁻¹). The compound was characterised by preparation of the picrate as a yellow solid from ethanol, m.p. – softened 135°-6°C, melted 139°-41°C(dec).

Found: C, 50.9%; H, 3.1%; N, 16.1%. C₁₂H₁₀N₂O·C₆H₃NO₇ requires: C, 50.9%; H, 2.6%; N, 16.5%.

Preparation of trans dichlorobis (ligand) rhodium(III) tetrachloro(ligand)rhodate(III) complexes.

Ethanolic (5 ml) solutions of rhodium trichloride trihydrate (τmM) and ligand (2 mM) were mixed. The resulting solution was heated under reflux for 30 min. The solid which deposited on cooling was filtered off and washed with ethanol. All other compounds described were vacuum desiccated over P₄O₁₀. This general method was used for the preparation of the following;

Trans-dichlorobis(di-2-pyridylketone)rhodium(III) tetrachloro(di-2-pyridylketone)rhodate(III). Yield 0.43 g.

Found: C, 40.5%; H, 3.3%; N, 8.7%. C₃₃H₂₄Cl₆N₆O₃Rh₂ requires: C, 40.8%; H, 2.5%; N, 8.7%.

Trans-dichlorobis(2-acetylpyridine)rhodium(III) tetrachloro(2-acetylpyridine)rhodate(III). Yield 0.38 g.

Found: C, 32.2%; H, 3.1%; N, 5.2%; Rh, 25.5%. C₂₁H₂₁Cl₆N₃O₃Rh₂ requires: C, 32.1%; H, 2.7%; N, 5.3%, Rh, 26.2%.

Trans-dichlorobis(2-m-aminobenzoylpyridine)tetrachloro(2-m-aminobenzoyl-pyridine)rhodate(III) trihydrate. Yield 0.20 g.

Found: C, 40.7%; H, 3.4%; N, 8.0%. C₃₆H₃₆Cl₆N₆O₆Rh₂ requires: C, 40.5%; H, 3.4%; N, 7.9%.

Addition of light petroleum (b.p. $100^{\circ}-120^{\circ}$ C) to the filtrate afforded a small quantity of a red solid identified as

Trans-dichloro(hydroxo)bis(2-m-aminobenzoylpyridine)rhodium(III) dihydrate. Found: C, 46.1%; H, 3.9%; N, 8.6%. C₂₄H₂₅Cl₂N₄O₅Rh requires: C, 46.2%; H, 4.0%; N, 8.9%.

Trans-dichlorobis(2-m-nitrobenzoylpyridine)rhodium(III) tetrachloro(2-m-aminobenzoylpyridine)rhodate(III) hexahydrate. Yield 0.36 g.

Found: C, 35.4%; H, 2.7%; N, 6.7%. C₃₆H₄₂Cl₆N₆O₉Rh₂ requires: C, 35.7%; H, 2.9%; N, 6.9%.

Trans-dichlorobis(2-m-aminobenzoylpyridine)rhodium(III) perchlorate hexahydrate. To a solution of rhodium(III) trichloride trihydrate (0.26 g, 1 mM) in ethanol (10 ml) was added an aqueous ethanolic solution (10 ml, 50% v/v) of 2-(*m*-aminobenzoyl)pyridine (0.4 g, 2 m*M*). The resulting solution was refluxed for 30 min. The orange product was filtered and washed with ethanol and water, yield 0.5 g.

Found: C, 36.9%; H, 30%; N, 7.2%. C₂₄H₃₂Cl₃N₄O₈Rh requires: C, 37.1%; H, 4.1%; N, 7.2%.

Trans-dichlorobis(2-m-nitrobenzoylpyridine)rhodium(III) perchlorate. The above method was used. On refluxing the solution for 30 min a red solid was produced, yield 0.25 g. This was identified as:

trans-dichloro(hydroxo)bis(2-m-nitrobenzoylpyridine)rhodium(III).

Found: C, 44.2%; H, 3.0%; N, 8.7%. $C_{24}H_{17}Cl_2N_4O_3Rh$ requires: C, 44.7%; H, 2.5%; N, 8.7%. Dilution of the filtrate with water afforded pale orange crystals of [Rh(pyCO C₆H₄NO₂)₂Cl₂]ClO₄, yield 0.22 g. The latter complex was also obtained by the metathesis of sodium perchlorate and the tetrachlororhodate salt in ethanol.

Found: C, 39,2%; H, 2.9%; N, 7.2%. C₂₄H₁₆Cl₃N₄O₂Rh requires: C, 39.5%; H, 2.2%; N, 7.7%.

Apparatus

Diffuse reflectante spectra were measured with Unicam SP 500 and 700 spectrophotometers fitted with their respective reflectance attachments. Infra-red spectra were measured for nujol mulls with Perkin Elmer 237 (4000-625 cm⁻¹), 225 (400-200 cm⁻¹) and Grubb Parsons DM4 (667-222 cm⁻¹) spectrophotometers. Conductance measurements were made with a Doran bridge. Solution spectra were determined with the SP 700 instrument.

RESULTS AND DISCUSSION

(a) Experiments with other nucleophiles

Concentrated aqueous solutions of alkali metal halides and cyanates were reacted with *trans*-[Rh(pyCOPh)₂Cl₂]ClO₄, but only hydroxodichlorobis(2-benzoylpyridine)rhodium(III) was obtained. However when potassium thiocyanate was used an impure orange material was obtained for which there was infra red evidence of thiocyanate co-ordination (ν (CN) = 2104 cm⁻¹). Dimethylformamide solutions of *trans*-[Rh(pyCOPh)₂Cl₂]ClO₄ (which thin layer chromatography showed to contain principally the orange isomer) were treated with potassium thiocyanate; there was no spectroscopic evidence for any reaction in this solvent.

(b) Complexes of other 2-pyridylketones

Eight new rhodium(III) complexes (Table I) were prepared to investigate the generality of the formation of the hydroxo-complex as a function of the ketonic ligand.

Di-2-pyridylketone when reacted with rhodium trichloride in the presence of ethanol affords *trans*-dichlorobis(di-2-pyridylketone)-rhodium(III) tetrachloro(di-2-pyridylketone)rhodate(III). The carbonyl frequency is characteristic of the uncoordinated group and the ligand is therefore NN co-ordinated². We found no evidence for linkage isomerism and do not consider this complex further in this paper. 2-Acetylpyridine gives an orange complex which we identify as *trans*-dichlorobis(2-acetylpyridine)rhodium(III) tetrachloro(2-acetylpyridine)-rhodate(III). We assign *trans*stereochemistry to this cation (and to [Rh(pyCOpy)₂Cl₂]⁺) on the basis of the

TABLE I						
Complex	Colour	Diffuse reflectance spectrum (kK)	$\nu(CO)cm^{-1}$	$\eta(OH) cm^{-1}$	v(RhCl)cm ⁻¹	$A_{M^{*}}(conc.)$
[Rh(pyCOpy)2Cl2] [Rh(pyCOpy)Cl4]	Yellow	22.0	(1705 1698 sh. 1694 1685 sh.	[355 m 335 s,sh. 325 s,b	51 (10 ⁻³ M)
[Rh(pyĊOMe) Cl2] [Rh(pyCOMe)Cl4]	Orange	21.7	(1572 sh. (1567 1563 sh.	I	370 s 332 s,b	51 (10 ⁻³ M)
[Rh(pyCO.C ₆ H ₄ ·NH ₂) ₂ Cl ₂] [Rh(pyCO.C ₆ H ₄ .NH ₂)Cl ₄]·3H ₂ O	Fawn	24.7 sh., 20.0 sh.	(1545 (1535 1530 sh.	mixed with \$\nt(NH)	332 s,b poor spectrum	$\begin{array}{c} 20 \ (10^{-8} \ M) \\ 29 \ (5 \ \times \ 10^{-4} \ M) \\ 49 \ (2.5 \ \times \ 10^{-4} \ M) \end{array}$
[Rh(pyCO.C ₆ H4.NO ₂)2Cl ₂] [Rh(pyCO.C ₆ H4.NO ₂)Cl ₄]·6H2O	Orange	23.5	(1545 sh. (1538 sh. (1525 sh.	3480 b	358 sh. 333 s,b	$\begin{array}{c} 36 \ (10^{-3} \ M) \\ 42 \ (5 \times 10^{-4} \ M) \\ 53 \ (2.5 \times 10^{-4} \ M) \end{array}$
[Rh(pyCO.C ₆ H ₄ NH ₂) ₂ Cl ₂]ClO ₄ ·6H ₂ O	Orange	26.3, 21.3 sh.	(1550 sh. 1545 1535 sh.	3500 b	poor spectrum	$\begin{array}{c} 31 \ (10^{-3} \ M) \\ 38 \ (5 \times 10^{-4} \ M) \\ 45 \ (2.5 \times 10^{-4} \ M) \end{array}$
[Rh(pyCO.C ₆ H4.NO ₈) ₅ Cl ₂]ClO ₄	Orange	23.0; 19.6 sh.	(1532 (1527 sh.	1	poor spectrum	$36 \ (10^{-3} \ M) \ 42 \ (5 \ imes \ 10^{-4} \ M) \ 54 \ (2.5 \ imes \ 10^{-4} \ M)$
[Rh(pyCO.C ₆ H ₄ . NH ₂) ₂ Cl ₂ .OH] · 2H ₂ O	Red		(1545 (1532 1515	mixed with \$\nu(NH)\$	poor spectrum	0 (10 ⁻³ M)
[Rh(pyCO.C ₆ H ₄ NO ₂) ₂ Cl ₂ .OH]	Red	22.2, 19.1	1530	3390	343 s	4 (10 ⁻³ M)
pyCOpy = di-2-pyridylketone; pyCOMe = pyridine.	= 2-acetyl	pyridine; pyCO.C ₆ H ₄ .NH ₂	$= 2 - (m - \operatorname{aminol})$	benzoyl)pyridine	pyCO.C ₆ H ₄ .NO ₂ =	= 2-(m-nitrobenzoyl)-

J. Less-Common Metals, 17 (1969) 53-57

56

pyinume.
* in dimethyl-formamide solution.

single sharp rhodium-chlorine stretching frequency at 370 cm⁻¹ (355 cm⁻¹, pyCOpy); the band at 332 cm⁻¹ being due to [Rh(pyCOMe)Cl₄]⁻, cf [Rh(pyCOPh)Cl₄]⁻¹. The compound resisted attempts to prepare the perchlorate, nor were we able to observe any tendency on the part of the cation to give a hydroxo-complex. The possibility that the different behaviour of the acetyl- and benzoylpyridine complexes might be due to the different electronic effects of the methyl and phenyl groups was then investigated by synthesis of the 2-(*m*-amino-) and (*m*-nitro-benzoyl)pyridine ligands. Reaction of these bases with ethanolic rhodium trichloride affords tetrachlororhodate(III) salts analogous to those considered above (Table I). Measurements of the molar conductivities of these, and of the corresponding perchlorate salts, indicate some degree of ion pairing in the dimethylformamide solutions. The complexes of 2-(m-aminobenzoyl)pyridine gave ill resolved far infra-red spectra. It was however possible to isolate neutral six co-ordinate hydroxocomplexes $[RhL_2Cl_2 \cdot OH]$ of both ligands (L) but the preparations were much more difficult than was the case with the 2-benzovlpyridine complexes (see experimental section). We were not able to isolate isomeric forms of the perchlorate complexes of these ligands but we did observe that solutions of $[RhL_2Cl_2]ClO_4$ (L = pyCOC_6H_4·NO₂, pyCOC_6H_4·NH₂) in nitromethane (orange) and in dimethylformamide (yellow) gave different spectra.

The results obtained suggest that the different behaviour of the 2-acetyl- and 2-benzovlpyridine complexes cannot be ascribed to the different electronic properties of the methyl- and phenyl-groups since neither substitution of the phenyl group with electron withdrawing or electron releasing groups prevents the formation of the hydroxocomplex, even though electronic spectra do seem sensitive to the group R (Fig. ii). The interpretation of the electronic spectra is not easy since, in many of the compounds, rhodium(III) is present in two different environments. The far infra-red spectra, however, suggest that the electronic effects transmitted to rhodium(III) by changing R (Fig. ii) are minimal. Thus ν (RhCl) is¹ at 372 cm⁻¹ for [Rh(pyCOPh)₂Cl₂]⁺ and at 370 cm⁻¹ for [Rh(pyCOMe)₂Cl₂]⁺; also [Rh(pyCOPh)₂Cl₂OH]¹ and $[Rh(pyCOC_6H_4 \cdot NO_2)_2Cl_2 \cdot OH]$ are seen to have identical spectroscopic properties. More probably, the different behaviour patterns observed for this series of rhodium(III) complexes of pyCOR may be attributed to differing solvent affects rather than to any electronic property of R.

We suggest that the mechanism of formation of the hydroxo complex follows the scheme of Fig. (i). The 6-hydrogen atoms of the cis-2-pyridyl-groups of the orange isomer would probably interfere thus facilitating a ring opening. A water molecule probably co-ordinates and deprotonates to afford the hydroxo-complex.

ACKNOWLEDGEMENTS

We thank Dr. G. C. KULASINGAM for discussion and for measurement of some spectra, also one of us (R.R.O.) thanks the S.R.C. for the award of a studentship.

REFERENCES

I R. R. OSBORNE AND W. R. MCWHINNIE, J. Chem. Soc. (A), (1968) 2153

R. R. OSBORNE AND W. R. MCWHINNIE, J. Chem. Soc. (A), (1967) 2075.
 A. R. HANDS AND A. R. KATRITZKY, J. Chem. Soc., (1958) 1754.

⁴ K. SCHOFIELD, J. Chem. Soc., (1949) 2408.