Preparation and Structures of Ruthenium(III) Complexes containing Tertiary Arsines, Tertiary Phosphines, and Isocyanides

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Preparation of the complexes $[RuCl_3(AsPh_3)_2(py)]$ and $[RuCl_3(PPh_3)_2(py)]$ (py = pyridine) is described. The latter has been treated with a variety of alkyl and aryl isocyanides at room temperature to produce complexes of general formula $[RuCl_3(PPh_3)(py)(CNR)]$. Dipole-moment measurements on $[RuCl_3(AsPh_3)_2(py)]$ confirm that it possesses a *mer* arrangement of the chloride groups and a *trans* arrangement of the arsines. Similar measurements show $[RuCl_3(AsPh_3)(bipy)]$ (bipy = 2,2′-bipyridyl) and $[RuCl_3(AsPh_3)(py)_2]$ to possess a *mer* arrangement of chloride groups with the pyridine molecules *cis* to one another in the latter complex.

A LARGE number of neutral, monomeric, ruthenium(III) complexes containing tertiary phosphines and arsines have been reported.[1-6] These fall into four distinct formula types: (*i*) $[RuCl_3(EPh_3)_2L]$ and $[RuBr_3(EPh_3)_2L]$ (E = As or P; L = a variety of alcohols, aldehydes, ketones, nitriles, and sulphides); [1-3] (*ii*) $[RuCl_3(EPh_3)L_2]$ and $[RuBr_3(EPh_3)L_2]$ [E = As or P; L = pyridine (py), 2-methylpyridine, or SMe_2]; [1-3] (*iii*) $[RuCl_3(EPh_3)(N\text{-}N)]$ and $[RuBr_3(EPh_3)(N\text{-}N)]$ [E = As or P; N-N = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)]; [3] and (*iv*) $[RuCl_3L_3]$ and $[RuBr_3L_3]$ (L = $AsMePh_2$,[4] $AsEt_2Ph$, PMe_2Ph, PEt_2Ph, $PBu^n{}_2Ph$, or PPh_3).[5,6]

In this paper we report two additional complexes of type (*i*), $[RuCl_3(AsPh_3)_2(py)]$ and $[RuCl_3(PPh_3)_2(py)]$, and the preparation of a new series of complexes having the general formula $[RuCl_3(PPh_3)(py)(CNR)]$ (CNR = a variety of alkyl and aryl isocyanides). In addition, dipole-moment measurements on representative complexes of formula types (*i*)—(*iii*) have been used to support structural assignments previously made on the basis of far-i.r. studies allied with electronic and e.s.r. spectral data.

TABLE 1

Analytical data for ruthenium(III) complexes

		Analysis (%)							
		Found				Calc.			
Complex	M.p. (θ_c/°C)	C	H	Cl	Other	C	H	Cl	Other
$[RuCl_3(AsPh_3)_2(py)]$	211—215	54.7	3.9	12.0	16.4 (As), 1.5 (N)	54.8	3.9	11.9	16.7 (As), 1.6 (N)
$[RuCl_3(PPh_3)_2(py)]$	179—182	60.6	4.3	13.1	7.4 (P), 1.9 (N)	60.7	4.4	13.1	7.6 (P), 1.7 (N)
$[RuCl_3(PPh_3)(py)(CNC_6H_4OMe\text{-}p)]$	154—156	54.3	4.0	15.7		54.5	4.0	15.6	
$[RuCl_3(PPh_3)(py)(CNCH_2Ph)]$	159—161	55.7	4.0	16.1		55.9	4.1	16.0	
$[RuCl_3(PPh_3)(py)(CNC_6H_4Me\text{-}o)]$	152—154	54.8	4.1			55.9	4.1		
$[RuCl_3(PPh_3)(py)(CNC_6H_{11})]$	154—155	54.7	4.7	16.4	4.7 (P), 4.2 (N)	54.7	4.7	16.2	4.7 (P), 4.3 (N)
$[RuCl_3(PPh_3)(py)(CNBu^t)]$	152—155	53.0	4.6	17.2		53.2	4.6	16.9	
$[RuCl_3(PPh_3)(py)(CNCH_2CHCH_2)]$	143—147	52.4	4.1	17.3		52.6	4.1	17.3	

RESULTS AND DISCUSSION

Preparation of $[RuCl_3(AsPh_3)_2(py)]$ *and* $[RuCl_3(PPh_3)_2(py)]$.—Although a wide variety of complexes of type (*i*) has been prepared, none has been reported in which L = pyridine. This is due to the strong binding ability of py which leads to substitution of more than one

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[6] J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

pyridine molecule into the co-ordination sphere of Ru^{III}. Thus, treatment of $[RuCl_3(AsPh_3)_2L]$ ($L =$ HOMe, HOEt, $OCMe_2$, or NCMe) with pyridine at room temperature typically leads to formation of $[RuCl_3(AsPh_3)(py)_2]$. However, when $[RuCl_3(AsPh_3)_2(HOMe)]$ was placed in pyridine and the reaction mixture *immediately* quenched by addition of a large excess of light petroleum the complex $[RuCl_3(AsPh_3)_2(py)]$ was precipitated. Analysis results for this complex and others prepared in this study are reported in Table 1.

Preparation of $[RuCl_3(PPh_3)_2(py)]$ was accomplished by prolonged treatment of $[RuCl_3(AsPh_3)(py)_2]$ with PPh_3 (1 : 2) in acetone at room temperature. The product was found to be a mixture of $[RuCl_3(PPh_3)(py)_2]$ and $[RuCl_3(PPh_3)_2(py)]$. These last two complexes were readily interconverted in acetone at room temperature which suggests the binding strengths of PPh_3 and py are comparable in these complexes.

Isocyanide Complexes of Ruthenium(III).—Ruthenium(III) complexes of general formula $[RuCl_3(PPh_3)(py)(CNR)]$ ($R = C_6H_4OMe$-*p*, CH_2Ph, C_6H_4Me-*o*, C_6H_{11}, Bu^t, or CH_2CHCH_2) were readily prepared by treating $[RuCl_3(PPh_3)_2(py)]$ with the appropriate isocyanide (1 : 1) in acetone at room temperature. Infrared frequencies in the isocyanide-stretching region are reported in Table 2. The observed frequencies are typical of isocyanide complexes of ruthenium in which both metal–ligand σ-bonding and π-bonding interactions are important.

TABLE 2

Infrared spectra (cm^{-1}) of $[RuCl_3(PPh_3)(py)(CNR)]$ in the isocyanide-stretching region

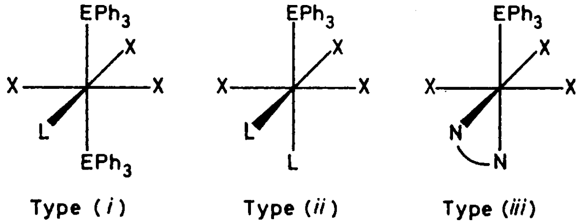
Complex	ν(NC)	
	complex [a]	free [b]
$[RuCl_3(PPh_3)(py)(CNC_6H_4OMe\text{-}p)]$	2 180	2 125
$[RuCl_3(PPh_3)(py)(CNCH_2Ph)]$	2 209	2 146
$[RuCl_3(PPh_3)(py)(CNC_6H_4Me\text{-}o)]$	2 174	2 122
$[RuCl_3(PPh_3)(py)(CNC_6H_{11})]$	2 201	2 138
$[RuCl_3(PPh_3)(py)(CNBu^t)]$	2 194	2 143
$[RuCl_3(PPh_3)(py)(CNCH_2CHCH_2)]$	2 209	

[a] All the spectra were taken in $CHCl_3$; values listed are accurate to ±1 cm^{-1}. [b] Values taken from L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley, New York, 1969.

These isocyanide complexes could also be prepared by reaction of $[RuCl_3(PPh_3)(py)_2]$ with the appropriate isocyanide. However, the yields were lower, and the products were contaminated with starting material. In contrast, we were unsuccessful in obtaining identifiable products from the interaction of $[RuCl_3(AsPh_3)_2(py)]$ and $[RuCl_3(AsPh_3)(py)_2]$ with isocyanides.

Dipole-moment Measurements.—Of the four formula types of neutral ruthenium(III) complexes outlined in the introduction the structures of type (*iv*), $[RuX_3L_3]$, have been most thoroughly investigated. Dipole-moment measurements and i.r. and e.s.r. studies have shown that the complexes $[RuCl_3L_3]$ ($L =$ a variety of phosphines and arsines,[5,7,8] thioethers,[8] pyridine,[8] substituted pyridines,[9] or NCMe [10]) all possess a meridional arrangement of the chloride groups and therefore also of the L groups. Far-i.r. and e.s.r. measurements have shown $[RuCl_3(py)_3]\cdot0.5C_6H_6$ and $[RuCl_3(NPhH_2)_3]\cdot0.5C_6H_6$ to be facial isomers.[10]

Structures of type (*i*)—(*iii*) complexes have also been proposed. Far-i.r. spectra of a number of type (*i*) complexes, $[RuX_3(EPh_3)_2L]$, have been investigated for cases in which X = Cl, E = As, and L = a series of alkyl and aryl cyanides.[3] In all the cases it was concluded that the chloride groups were *mer* with a *trans* arrangement of the arsine groups preferred but not proven.[3,11]



Type (*i*) Type (*ii*) Type (*iii*)

Structures of $[RuX_3(EPh_3)_2L]$, $[RuX_3(EPh_3)L_2]$, and $[RuX_3(EPh_3)(N\text{–}N)]$

Among complexes of formula type (*ii*) only $[RuCl_3(EPh_3)(py)_2]$ (E = As or P) have been investigated.[3] Far-i.r. evidence again indicates a *mer* arrangement of chlorides. The *cis* arrangement of the pyridine molecules is suggested because of the similarity of the electronic and e.s.r. spectra of $[RuCl_3(EPh_3)(py)_2]$ and $[RuCl_3(EPh_3)(N\text{–}N)]$ (E = As or P; N–N = bipy). The latter complex and $[RuCl_3(EPh_3)(phen)]$ have been assigned the structure shown above based on an analysis of their far-i.r. spectra.[3]

Dipole-moment measurements strongly support the structure assignments shown above. Table 3 lists the measured dipole moments of $[RuCl_3(AsPh_3)_2(py)]$, $[RuCl_3(AsPh_3)(py)_2]$, and $[RuCl_3(AsPh_3)(bipy)]$, representing formula types (*i*), (*ii*), and (*iii*) respectively. The dipole moments of other complexes prepared in this study were not determined either because the complexes were known to undergo dissociation in benzene solution [1] or because of their limited solubility in benzene. Comparison of these results with dipole moments of complexes of Ru^{II}

TABLE 3

Dipole moments of some ruthenium complexes in in benzene at 25 °C

Complex	Formula type	μ/D
$[RuCl_3(AsPh_3)_2(py)]$	(*i*)	7.54
$[RuCl_3(AsPh_3)(py)_2]$	(*ii*)	7.69
$[RuCl_3(AsPh_3)(bipy)]$	(*iii*)	7.6

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[7] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

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[11] L. Ruiz-Ramirez and T. A. Stephenson, *J.C.S. Dalton*, 1975, 2244.

and Ru^{III} with established structures [1,5,12-14] clearly indicates that the structures of the three complexes are as shown above.

EXPERIMENTAL

Chemicals used in this study were reagent grade or equivalent except for ' ruthenium trichloride trihydrate ' which was purchased from Fisher Scientific Company and used without purification. All the reactions were conducted in a nitrogen atmosphere, and exposure of products in solution to air was minimized. Microanalyses were by Galbraith Laboratories, Knoxville, Tennessee. Melting points were determined on a Fisher–Johns block and are corrected. Routine i.r. spectra were recorded in the 625—4 000 cm^{-1} region on a Beckman IR 8 spectrophotometer; spectra of the complexes $[RuCl_3(PPh_3)(py)(CNR)]$ in the isocyanide-stretching region were taken on a Beckman IR 20 spectrophotometer calibrated using the rotational spectrum of CO.

Trichloro(pyridine)bis(triphenylarsine)ruthenium(III).—The complex $[RuCl_3(AsPh_3)_2(HOMe)]$ (0.20 g) was dissolved in pyridine (3 cm^3). Excess of light petroleum (b.p. 60—90 °C) was added *immediately* to precipitate light green crystals of the complex. The crystals were washed with light petroleum and hot acetone, and dried *in vacuo* (29% yield).

Trichloro(pyridine)bis(triphenylphosphine)ruthenium(III).—The complex $[RuCl_3(AsPh_3)(py)_2]$ (0.14 g, 0.20 mmol) was dissolved in acetone (30 cm^3) and triphenylphosphine (0.11 g, 0.41 mmol) was added. After stirring at room temperature for 24 h, green crystals of the complex were recovered, washed with acetone, and dried *in vacuo* (29% yield).

*Trichloro(*p*-methoxyphenyl isocyanide)(pyridine)(triphenylphosphine)ruthenium*(III).—The complex $[RuCl_3(PPh_3)_2(py)]$ (0.068 g, 0.084 mmol) was dissolved in acetone (40 cm^3) and 4.2×10^{-3} mol dm^{-3} *p*-methoxyphenyl isocyanide (20 cm^3, 0.084 mmol) in acetone was added. After stirring at room temperature for *ca.* 10 min, the colour of the solution changed from green to orange. Stirring was continued for a total of 45 min and the volume of solvent reduced to 10 cm^3 to precipitate the product, which was recrystallized from acetone–light petroleum (yield 68%).

*(Benzyl isocyanide)trichloro(pyridine)(triphenylphosphine)-trichloro(pyridine)(*o*-tolyl isocyanide)(triphenylphosphine)-, trichloro(cyclohexyl isocyanide)(pyridine)(triphenylphosphine)-, trichloro(pyridine)(t-butyl isocyanide)(triphenylphosphine)-,* and *(allyl isocyanide)trichloro(pyridine)(triphenylphosphine)-ruthenium*(III) were prepared in the manner described above for $[RuCl_3(PPh_3)(py)(CNC_6H_4\text{-}OMe\text{-}p)]$.

Trichlorobis(pyridine)(triphenylarsine)- and *(2,2′-bipyridine)trichloro(triphenylarsine)-ruthenium*(III) were prepared as reported previously.[1]

Dipole-moment Measurements.—Dipole-moment measurements were made in benzene solvent at 25 °C using a Kahl Scientific model DM 01 dipolemeter. Atom polarization was taken to be 15% of electron polarization. The dipole moments given in Table 3 are accurate to ±0.2D.* Experimental data used in the calculations were as follows: †

	$[RuCl_3(AsPh_3)_2(py)]$	$[RuCl_3(AsPh_3)(py)_2]$	$[RuCl_3(AsPh_3)(bipy)]$
$\Delta\varepsilon/f_2$	8.06	10.37	9.46 *
$-\Delta v/f_2$	0.717	0.675	0.655 *
w_1/w_2	1 038.4	320.26	3 636.2
η	1.498 1	1.498 3	1.498 2
d	0.874 09	0.875 02	0.873 86
$T^{P}{}_{2}$	1 476	1 405	1 289 *
$E^{P}{}_{2}$	274	171	101
$O^{P}{}_{2}$	1 161	1 208	1 173
μ/D	7.54	7.69	7.6

* Probably somewhat low; in all the measurements a small amount of $[RuCl_3(AsPh_3)(bipy)]$ remained undissolved.

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* Throughout this paper: 1 D ≈ 3.34×10^{-30} C m.

† Symbols are defined by B. L. Shaw in ' Physical Methods in Organic Chemistry,' ed. J. C. P. Schwarz, Holden-Day, San Francisco, 1964, pp. 323—326.

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