

Ruthenium(II) Complexes Containing Nitrogen Heterocyclics†

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Fifteen new complexes of the type $\text{RuHClCO}(\text{PPh}_3)_2(\text{L})$ where L is a nitrogen containing heterocyclic base, have been synthesised by the reaction between $\text{RuHClCO}(\text{PPh}_3)_3$ [1] and excess of L. These complexes have been characterised by elemental analyses, IR and ^1H NMR spectral data. Our studies reveal the following order of affinities of various ligands for Ru(II): 4-vinylpyridine > 4-picoline > 3-cyanopyridine > 2,2'-bipyridyl $\approx$ 1,10-phenanthroline > benzo[f]quinoline > quinazolines. Ruthenium(II) complexes of pyridine derivatives exist as isomers in which the pyridine base is situated *trans* to either carbonyl or hydride ligand.

The unusual *trans*-bond weakening effect of the hydride ligand in $\text{RuHClCO}(\text{PPh}_3)_3$ [1] accounts for the ready displacement of *trans* phosphine by strongly bonding Lewis bases. Substitution reaction of [1] using phosphines, phosphites, phosphonites, phosphinates and 4-vinylpyridine have been recently studied¹⁻³. Shaw *et al.*⁴ found that no detectable displacement of phosphine was observed when 4-methylpyridine was added in excess to $\text{RuHClCO}(\text{Pr}_2\text{PhP})_3$ and suggested the following order of 'coordinating affinities' for group V donors with class 'b' metals: $\text{N} \ll \text{P} > \text{As}$. We have observed that heterocyclic nitrogen bases can easily replace *trans* phosphine group in the complex [1] giving substitution products in good yields.

Materials and Methods

All the reactions were carried out under nitrogen atmosphere using Schlenk tube technique. The solvents were purified and dried using standard procedures, distilled and degassed before use. Nitrogen bases were dried over KOH pellets and were freshly distilled in vacuum. The complex $\text{RuHClCO}(\text{PPh}_3)_3$ was prepared by the procedure reported in literature⁷.

Compounds were analysed for elements at the Micro-Analytical Section of our Laboratory. The IR spectra were recorded in nujol, KBr or in chloroform on a Perkin-Elmer Model 599 IR spectrophotometer. ^1H NMR spectra were obtained on a Bruker WH 90 spectrometer.

Carbonylchlorohydrido(4-methylpyridine)-bis (triphenylphosphine)ruthenium (II)

$\text{RuHClCO}(\text{PPh}_3)_3$ (0.24 g; 0.25 mmol) was added to benzene (20 ml) containing 4-methylpyridine (0.5 ml)

and the mixture was stirred at ambient temperature for 24 h. The green solution was concentrated *in vacuo* and the separated solid was washed with hexane, ether to get a green microcrystalline solid (70%).

Other compounds listed in Table 1 were similarly prepared using excess of the ligand and $\text{RuHClCO}(\text{PPh}_3)_3$ in benzene.

Results and Discussion

The hydrido complex [1] reacts with nitrogen donor ligands in benzene or tetrahydrofuran solution at ambient temperature ($\sim 25^\circ$) to afford the substitution products $\text{RuHClCO}(\text{PPh}_3)_2(\text{L})$ as light coloured air-stable solids, soluble in most organic solvents. The ligands used are pyridine, 4-vinylpyridine, 4-methylpyridine, 3-cyanopyridine, 2-benzylpyridine, pyridine-2-carbinol, 2-*m*-xylylpyridine, piperidine, morpholine, 2,2'-bipyridyl, 1,10-phenanthroline, benzo[f]quinoline, isonicotonic acid hydrazide, 4-phenyl-6-chloroquinazoline and 4-phenyl-6,7-dimethoxyquinazoline (Table 1).

The IR spectra (Table 2) of complexes $\text{RuHClCO}(\text{PPh}_3)_2(4\text{-Vp})$ and $\text{RuHClCO}(\text{PPh}_3)_2(4\text{-Mepy})$ show $\nu(\text{Ru-H})$ at $\sim 1985\text{ cm}^{-1}$ suggesting a reduced Ru-H bond order, whereas all other complexes exhibit medium or weak band above 2000 cm^{-1} . A reduction in $\nu(\text{C}\equiv\text{O})$ suggests increased Ru-CO $d_\pi-p_\pi$ back bonding in these complexes since the nitrogen donor ligand is a strong σ -donor and a poor π -acceptor than triphenylphosphine. Pyridine and substituted pyridine derivatives show a characteristic $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ vibration around 1600 cm^{-1} . A medium band around 995 cm^{-1} is assigned to the breathing mode of pyridine ring^{5,6} which is shifted to higher frequencies ($\sim 1025\text{ cm}^{-1}$) suggesting the coordination of nitrogen. However, the starting

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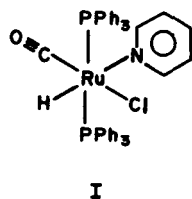
Table 1—New Ruthenium(II) Complexes Containing Nitrogen Heterocyclics

Sl No.	Compound, $\text{RuHClCO}(\text{PPh}_3)_2(\text{L})$, where L =	Yield (%)	Colour, m.p. ($^{\circ}\text{C}$)	Found(Calc.), %		
				C	H	N
1	Pyridine	65	Green 175	65.51(65.57)	4.59(4.71)	1.78(1.82)
2	4-Vinylpyridine	78	Colourless 199	66.51(66.44)	4.89(4.81)	1.67(1.76)
3	4-Methylpyridine	70	Green 214	65.78(65.94)	4.78(4.89)	1.80(1.78)
4	3-Cyanopyridine	71	Yellow 190	65.08(65.02)	4.34(4.44)	3.51(3.52)
5	2-Benzylpyridine	60	Brown low melting	68.32(68.47)	5.14(5.04)	1.65(1.63)
6	Pyridine-2-carbinol	75	Yellow > 250	64.49(64.54)	4.80(4.88)	1.71(1.75)
7	2- <i>m</i> -xylpyridine	69	Grey 90	68.80(68.74)	5.11(5.04)	1.61(1.60)
8	Piperidine	60	Pink 117	64.95(65.06)	5.51(5.42)	1.75(1.81)
9	Morpholine	65	Brown 185	63.28(63.35)	4.97(5.15)	1.71(1.80)
10	2,2'-Bipyridyl*	80	Pink 195	65.21(65.01)	4.76(4.75)	3.18(3.24)
11	1,10-Phenanthroline*	75	Yellow 179	66.15(66.23)	4.53(4.62)	3.06(3.15)
12	Benzo[<i>f</i>]quinoline	55	Brown non-melting	68.99(69.07)	4.61(4.64)	1.54(1.61)
13	Isonicotinic acid hydrazide	80	Yellow 105	62.57(62.42)	4.52(4.63)	5.04(5.08)
14	4-Phenyl-6-chloroquinazoline	72	Brown 125	65.70(65.81)	4.23(4.33)	2.93(3.01)
15	4-Phenyl-6,7-dimethoxy-quinazoline	60	Brown 170	66.62(66.52)	4.65(4.71)	2.85(2.94)

*Product contained one water molecule.

hydrido complex also shows a weak band at 1030 cm^{-1} which makes the interpretation difficult.

The high field ^1H NMR spectrum of the pyridine complex (Table 2) comprises a triplet centered at $-\delta$ 13.53 with $^2J(\text{PH})_{\text{cis}} = \sim 20\text{ Hz}$ suggesting both the phosphorus atoms are *trans* to each other. Hence the stereochemistry of the complex is suggested to be as shown below (I):



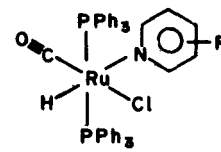
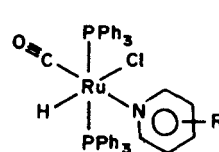
However, the ring substituted pyridine derivatives exhibit two triplets due to Ru-H resonance which explains the presence of two isomers. The resonance due to methyl protons of the complex $\text{RuHClCO}(\text{PPh}_3)_2$ (4-Mepy) is observed at a higher magnetic field, δ 2.05, compared to that for the free ligand at δ 2.30. On the basis of the NMR integration data the ratios of the two isomers (a and b) for 4-methylpyridine, 4-vinylpyridine, 3-cyanopyridine, pyridine-2-carbinol and isonicotinic acid hydrazide ruthenium complexes are *ca.* 1:7, 1:16, 1:1, 2:1 and 1.1:1 respectively. These data suggest the stereochemistry of isomers a and b as shown in IIa and IIb.

The adducts obtained by the reaction of 1,10-phenanthroline and 2,2'-bipyridyl show monodentate

Table 2—Spectral Data for New Ruthenium(II) Complexes

Sl No.*	IR frequency (cm^{-1})		^1H NMR chemical shift (δ ppm)
	$\nu(\text{Ru-H})$	$\nu(\text{C}\equiv\text{O})$	
1	2010	1925, 1915	—13.53 ^a
2	1990	1900	—12.4 ^a , —13.52 ^b
3	1985	1900, 1920	—12.44 ^a , —13.55 ^b , CH_3 2.05
4	2020	1910, 2230 ($\text{C}\equiv\text{N}$)	—13.60 ^a , —13.46 ^b
5	2030	1925	—10.05 ^a , —15.10 ^b , CH_2 4.70
6	1930	1910	—4.47 ^t
7	2030	1920	—13.70 ^t
8	2020	1915	—13.50 ^t
9	2010	1920	—11.35 ^t
10	1980	1920	—11.09 ^t
11	2020	1920	—
12	2000	1930, 1910	—13.55 ^a , —14.46 ^b
13	2030	1915	—
14	2040	1940	—
15	2040	1935	—

*Sl. Nos are same as in Table 1; in $\text{RuHClCO}(\text{PPh}_3)_3$, $\nu(\text{Ru-H})$ occurs at 2020 m , $\gamma(\text{C}\equiv\text{O})$ at 1922 s and 1903 sh cm^{-1} ; a and b refers to isomers a and b.



$\text{R} = 4\text{-CH:CH}_2, 4\text{-CH}_3, 3\text{-CN}, 2\text{-CH}_2\text{OH}, 4\text{-CONHNH}_2$

nature of the ligand; the second nitrogen coordinates to one water molecule as shown by elemental analysis, IR and ^1H NMR studies. Downfield shift observed for the Ru-H proton suggests considerable $d_{\pi}-p_{\pi}$ backbonding operating in these heterocyclic ligands compared to that in simple pyridine derivatives. However, ^1H NMR spectra of benzo[f]quinoline and quinazoline derivatives did not show resonance due to Ru-H suggesting decomposition of the complex in solution as these ligands are much weaker than pyridine bases.

References

- 1 Creswell C J, Robinson S D & Sahajpal A, *Polyhedron*, **12** (1983) 517.
- 2 Gilje J W, Schmutzler R, Sheldrick W S & Wray V, *Polyhedron*, **2** (1983) 603.
- 3 Gopinathan S, Unny I R & Gopinathan C, *Polyhedron* (in press).
- 4 Douglas P G & Shaw B L, *J chem Soc, A* (1970) 1556.
- 5 Singh N K, Agarwal N & Aggarwal R C, *Indian J Chem*, **24A** (1985) 617.
- 6 Plytzanopoulos M, Pneumatikakis E, Hadjiliedis N & Katakis D, *J inorg nucl Chem*, **39** (1977) 965.
- 7 Ahmed N, Levison J J, Robinson S D & Uttley M F, *Inorganic syntheses*, Vol. 15 (McGraw Hill, New York) 1974.