

Ruthenium(II) & rhodium(I) complexes of 2-hydroxypyridines†

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Received 9 May 1988; revised and accepted 18 July 1988

Ruthenium(II) and rhodium(I) precursors namely $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$, $[\text{RuCl}_2(\text{PPh}_3)_3]$ and $[\text{RhH}(\text{PPh}_3)_4]$ react with 2-hydroxypyridine (PyOH) and 6-methyl-2-hydroxypyridine (MePyOH) to afford a range of novel mononuclear complexes, namely $[\text{RuCl}(\text{CO})(\text{PyO})(\text{PPh}_3)_2]$, $[\text{RuH}(\text{CO})(\text{PyO})(\text{PPh}_3)_2]$, $[\text{RuCl}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2]$, $[\text{RuH}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2]$, $[\text{Ru}(\text{MePyO})_2(\text{PPh}_3)_2]$, $[\text{Ru}(\text{CO})_2(\text{PyO})_2]$, $[\text{Rh}(\text{PyO})(\text{PPh}_3)_2]$ and $[\text{Rh}(\text{MePyO})(\text{PPh}_3)_2]$. In these complexes the oxy-pyridines are bound in bidentate (N,O-chelate) mode. The complexes have been characterised by analytical, IR and ^1H NMR data. Evidences indicate that $[\text{RuH}/\text{Cl}(\text{CO})(\text{PyO}/\text{MePyO})(\text{PPh}_3)_2]$ complexes exist in two geometrical isomeric forms.

Chromium, molybdenum, tungsten¹, ruthenium² and rhodium³ are reported to form binuclear compounds of composition $\text{M}_2(\text{MePyO})_4$, where MePyO represents the anion of 2-hydroxy-6-methylpyridine. In these binuclear complexes each ligand moiety is coordinated to two metal atoms⁴. The mononuclear complex $[\text{Ru}(\text{PyO})(\text{PPh}_3)_2]$ has been synthesised and studied by Wilkinson *et al.*⁵ who have assigned *cis* coordination of hydroxypyridine anion through oxygen and nitrogen atoms. In continuation of our work on chelated ruthenium(II) complexes⁶ we now report the synthesis and characterisation of mononuclear ruthenium(II) and rhodium(I) complexes of 2-hydroxypyridine and 2-hydroxy-6-methylpyridine.

Experimental

2-Hydroxypyridine (PyOH) and 2-hydroxy-6-methylpyridine (MePyOH) were obtained from M/s Aldrich Chemical Co., USA. The complexes $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{PPh}_3)_4$ were synthesised by literature procedures⁷. The "red carbonyl solution", $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$, was freshly prepared by the reaction of carbon monoxide gas with an ethanolic solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (refs 8,9). Reagent grade solvents were dried and distilled before use. Tetrahydrofuran (THF) (Loba Chemie, Bombay)

was distilled over sodium-benzophenone complex under nitrogen just before use.

Synthesis of $\text{RuH}(\text{CO})(\text{PyO})(\text{PPh}_3)_2$

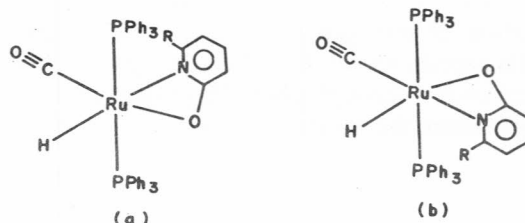
Sodium derivative of 2-hydroxypyridine was prepared by stirring for 30 min a solution containing sodium methoxide (0.054 g; 0.001 mol) in methanol and PyOH (0.095 g; 0.001 mole). From the clear solution, methanol was removed under reduced pressure and the product digested with THF (~30 ml). To this was added $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.238 g; 0.00025 mole) and the resulting white slurry was stirred for 24 hr at room temperature. The solution was concentrated to dryness and the residue extracted with benzene (25 ml) and centrifuged to remove sodium chloride formed in the reaction. The clear benzene solution was concentrated to crystallisation when colourless crystals were obtained; these crystals were washed with diethyl ether and dried *in vacuo*, yield 0.150 g (80%), m.p. 220°. The complexes $\text{RuH}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{CO})_2(\text{PyO})_2$ were similarly prepared.

Synthesis of $\text{RuCl}(\text{CO})(\text{PyO})(\text{PPh}_3)_2$

To a benzene solution (25 ml) of PyOH (0.0238 g; 0.00025 mole) was added $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.238 g; 0.00025 mole) and stirred for 24 hr at room temperature. The yellow solution was concentrated to about 5 ml, cooled to yield a yellow microcrystalline solid mass which was filtered off, washed with diethyl ether and dried *in vacuo*, yield 0.166 g (85%), m.p. 240°(d). Similarly was prepared $\text{RuCl}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2$; $\text{Rh}(\text{PyO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{MePyO})(\text{PPh}_3)_2$ were prepared by a similar reaction between $\text{RhH}(\text{PPh}_3)_4$ and PyOH or MePyOH.

Results and Discussion

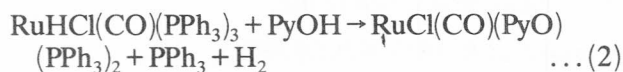
The reaction between $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and PyONa or MePyONa in THF (Eq. 1) affords two isomeric products (a and b) having the formula $\text{RuH}(\text{CO})(\text{PyO}/\text{MePyO})(\text{PPh}_3)_2$.



R = H, CH₃

†NCL Communication No. 4442

The isomers could not be separated by chromatographic methods. The chloro complexes $\text{RuCl}(\text{CO})(\text{PyO}/\text{MePyO})(\text{PPh}_3)_2$ were prepared by the reaction between $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and the above two hydroxypyridines in benzene (Eq. 2).



These complexes are also formed as mixtures of isomeric compounds. The IR spectra of the hydrido complexes (Sl nos 1 and 2, Table 1) in nujol, exhibit two medium bands at 1930 and 1965 cm^{-1} , respectively due to $\nu(\text{Ru}-\text{H})$. The terminal $\nu(\text{C}\equiv\text{O})$ appears at 1910 cm^{-1} as compared to those of the chloro complexes [Sl nos 3 and 4, Table 1] which appear at 1940 and 1915 cm^{-1} respectively. This shift in $\nu(\text{C}\equiv\text{O})$ of the hydrido complexes could be attributed to the presence of strongly σ -donating hydride ligand thereby increasing metal-carbon π interaction. In the complex $\text{Ru}(\text{CO})_2(\text{PyO})_2$ two broad bands are observed at 2025 and 1970 cm^{-1} due to $\nu(\text{C}\equiv\text{O})$ suggesting the presence of *cis* carbonyl ligands.

The complexes exhibit bands due to pyridine ring vibrations ($\text{C}=\text{C}/\text{C}=\text{N}$ stretching) at 1590 and 1550 cm^{-1} (ref. 10). In the 1400-1450 cm^{-1} region triphenylphosphine also gives strong absorption bands. The CH out-of-plane bending vibrations are observed in the region of 750-760 cm^{-1} while in the free ligands these appear at $\sim 730 \text{ cm}^{-1}$. The shift of CH out-of-plane mode to higher wavenumber is probably due to coordination of pyridine ring nitrogen to ruthenium.

High field ^1H NMR spectrum of $\text{RuH}(\text{CO})(\text{PyO})(\text{PPh}_3)_2$ displays two triplets of equal intensities at $\delta -11.71$ and -16.92 ppm which clearly indicate the presence of two isomers. A coupling constant of $^2J(\text{PH})_{\text{cis}} = 20$ Hz suggests that both the phosphine groups are *cis* to hydride and they are mutually *trans* in the hexacoordinated ruthenium complex. Similar sets of triplets are observed in the case of $\text{RuH}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2$ due to presence of isomers. The methyl protons in the above 2-hydroxy-6-methylpyridine derivatives resonate at higher field ($\delta 2.4$ ppm) as compared to those of the free ligand. A shift to lower field would have been expected on the basis of strong σ -donation of nitrogen lone pair to ruthenium. But model studies reveal that when the ligand is bonded to ruthenium through phenolic oxygen and ring nitrogen atom, the methyl group comes in the neigh-

Table 1—New ruthenium(II) and rhodium(I) complexes of 2-hydroxypyridine (PyOH) and 2-hydroxy-6-methylpyridine (MePyOH)

Sl No. Compound (colour)	m.p. ($^{\circ}\text{C}$)	Found (calc.), %		
		C	H	P
1 $\text{RuH}(\text{CO})(\text{PyO})(\text{PPh}_3)_2$ (colourless)	220	67.49 (67.37)	4.80 (4.71)	8.19 (8.27)
2 $\text{RuH}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2$ (colourless)	265	67.68 (67.70)	4.78 (4.80)	8.08 (8.12)
3 $\text{RuCl}(\text{CO})(\text{PyO})(\text{PPh}_3)_2$ (yellow)	240	64.38 (64.47)	4.30 (4.38)	7.93 (7.91)
4 $\text{RuCl}(\text{CO})(\text{MePyO})(\text{PPh}_3)_2$ (yellow)	260	64.87 (64.78)	4.67 (4.55)	7.68 (7.77)
5 $\text{Ru}(\text{CO})_2(\text{PyO})_2$ (grey)	220	41.68 (41.74)	2.46 (2.33)	—
6 $\text{Ru}(\text{PyO})_2(\text{PPh}_3)_2$ (yellow)	275	67.78 (67.89)	4.64 (4.71)	7.70 (7.61)
7 $\text{Ru}(\text{MePyO})_2(\text{PPh}_3)_2$ (pink)	197	68.55 (68.48)	4.96 (5.03)	7.35 (7.36)
8 $\text{Rh}(\text{PyO})(\text{PPh}_3)_2$ (yellow)	134	68.33 (68.25)	4.67 (4.75)	8.63 (8.59)
9 $\text{Rh}(\text{MePyO})(\text{PPh}_3)_2$ (colourless)	141	68.46 (68.58)	4.84 (4.93)	8.49 (8.42)

bourhood of one of the phenyl rings of the triphenylphosphine and the ring current diamagnetism on the methyl protons results in the shift of these protons to higher field. Two singlets are observed for methyl protons again suggesting the presence of two isomers. There is no downfield shift of methyl resonance in the square planar rhodium(I) complex $\text{Rh}(\text{MePyO})(\text{PPh}_3)_2$ as expected.

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