

(Imidazole)(dicarbonyl)rhodium(I) Complexes

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Five-coordinate Rh(I) compounds of the type, $[\text{Rh}(\text{CO})_2\text{L}_2\text{Cl}]$ (where L = imidazole or substituted imidazoles) have been prepared and characterized by elemental analyses, conductivity measurements and IR data.

The dimeric compound $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ has been used as a starting material for the synthesis of a number of rhodium(I) compounds¹⁻⁴. Five-coordinate rhodium(I) dicarbonyl compounds with triphenylphosphine, pyridine or benzimidazole have been reported earlier⁵⁻⁸. Recently we have reported a number of rhodium(I) compounds with various substituted imidazoles and triphenylphosphine⁹. Spectral study of a mixture containing 1-methylimidazole and the dimer $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ has been reported¹⁰. In an attempt to study the reactions of imidazoles with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ we obtained some five-

coordinate complexes of rhodium(I), which are described in this note.

$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (Arora-Matthey) was evaporated with conc. HCl several times before use. The ligands (Fluka or BASF) used were: imidazole (Im), 1-methylimidazole (1-MeIm), 1-vinylimidazole (1-VIm), 1-vinyl-2-methylimidazole (1-V-2-MeIm), 1-n-butylimidazole (1-n-BuIm), 2-methylimidazole (2-MeIm), 2-ethylimidazole (2-EtIm), 2-isopropylimidazole (2-i-PrIm), 2-ethyl-4(5)-methylimidazole (2-Et-4(5)-MeIm), 1,2-dimethylimidazole (1,2-Me₂Im) and 4-methylimidazole (4-MeIm). The solvents were purified by standard methods. The dimer $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared by the literature method¹¹. The molar conductances were measured in DMSO using a Systronics DRC bridge type 303.

The compounds were prepared by adding a solution of the ligand (4 mmol) in acetone (20 ml) to a solution of the dimer (1 mmol) in acetone (20 ml) with constant stirring. On mixing, the colour of the reaction mixture changed from red to yellow with simultaneous precipitation of a yellow compound in certain cases. The solution was concentrated *in vacuo*, stirred again with acetone and filtered. The compounds are

Table I—Characterisation Data of Five-coordinate Rh(I) Complexes

Compound	Found (Calc.), %					Decomp. point °C
	C	H	N	Cl	Rh	
$\text{Rh}(\text{CO})_2\text{Im}_2\text{Cl}$	27.55 (29.06)	3.00 (2.42)	17.10 (16.95)	11.20 (10.73)	— —	260-70 —
$\text{Rh}(\text{CO})_2(1\text{-MeIm})_2\text{Cl}$	32.70 (33.48)	4.22 (3.34)	15.20 (15.63)	10.10 (9.89)	29.20 (28.71)	230-50 —
$\text{Rh}(\text{CO})_2(1\text{-VIm})_2\text{Cl}$	36.60 (37.60)	3.57 (3.23)	13.48 (14.64)	10.14 (9.87)	27.43 (26.91)	300 —
$\text{Rh}(\text{CO})_2(1\text{-V-2-MeIm})_2\text{Cl}$	39.50 (40.94)	4.70 (3.89)	12.22 (13.64)	9.50 (8.63)	25.60 (25.07)	250-70 —
$\text{Rh}(\text{CO})_2(1\text{-n-BuIm})_2\text{Cl}$	42.70 (43.40)	6.23 (5.42)	12.57 (12.60)	8.55 (8.01)	23.35 (23.26)	143 —
$\text{Rh}(\text{CO})_2(2\text{-MeIm})_2\text{Cl}$	32.75 (33.48)	3.58 (3.34)	14.88 (15.62)	10.28 (9.89)	— —	210 —
$\text{Rh}(\text{CO})_2(2\text{-EtIm})_2\text{Cl}$	36.80 (37.27)	5.38 (4.14)	15.33 (14.49)	9.36 (9.17)	— —	300 —
$\text{Rh}(\text{CO})_2(2\text{-i-PrIm})_2\text{Cl}$	39.90 (40.54)	5.20 (4.82)	13.30 (13.51)	9.20 (8.85)	25.21 (24.83)	240 —
$\text{Rh}(\text{CO})_2(2\text{-Et-4(5)-MeIm})_2\text{Cl}$	39.30 (40.54)	5.80 (4.82)	12.50 (12.51)	9.32 (9.55)	25.10 (24.83)	235 —
$\text{Rh}(\text{CO})_2(1,2\text{-Me}_2\text{Im})_2\text{Cl}$	36.80 (37.27)	4.45 (4.14)	14.92 (14.49)	10.44 (10.17)	27.50 (26.93)	252 —
$\text{Rh}(\text{CO})_2(4\text{-MeIm})_2\text{Cl}$	32.50 (33.48)	3.83 (3.34)	16.10 (15.62)	10.10 (9.89)	— —	200 —

sparingly soluble in most of the solvents but soluble in DMSO.

The characterisation data of the complexes are recorded in Table I. Most of the compounds decompose without melting and behave as non-electrolytes in DMSO (Λ_M in the range of 3.0 to 15.7 ohm⁻¹ cm² mol⁻¹). The IR spectra of the complexes were recorded in nujol. Two very strong ν_{CO} modes without any splitting have been observed in the IR spectra of all the compounds at ~ 2070 and ~ 2000 cm⁻¹. The bands appear at higher wave numbers as compared to those observed in some five-coordinate rhodium(I) compounds containing *cis*-carbonyl group⁵. The substituents on imidazole moiety do not appear to have any effect on ν_{CO} mode. The ν_{Rh-Cl} modes in the complexes appear at ~ 290 cm⁻¹, in conformity with ν_{Rh-Cl} of rhodium (I) compounds containing triphenylphosphine ligands¹.

It may be noted that in the preparation of the complexes of Rh(I), the molar ratio of dimer:ligand should be strictly maintained as indicated i.e. 1:4 (dimer:ligand). If the ligand is added to the dimer in 2:1

proportion, then a mixed compound partly red and partly yellow in colour is obtained. When the ligand is in more than 4-fold excess over the dimer, a four coordinate compound RhL_3Cl is obtained.

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