

Cationic Carbonyl Complexes of Rh(I) with Imidazoles

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Cationic complexes of rhodium(I) of the type $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$ (L is Ph_3P or Ph_3As) react with imidazoles to give four-coordinate complexes of the type $[\text{Rh}(\text{CO})\text{YL}_2]\text{ClO}_4$ and five-coordinate complexes of the type $[\text{Rh}(\text{CO})(\text{Y}-\text{Y})\text{L}_2]\text{ClO}_4$ [Y is imidazole, benzimidazole or substituted benzimidazole and (Y-Y) is 2-(α -pyridyl)benzimidazole]. Complexes of the types $[\text{Rh}(\text{CO})_2(\text{Y}-\text{Y})]\text{ClO}_4$ and $[\text{Rh}(\text{CO})_2(2\text{-phenylbenzimidazole})_2]\text{ClO}_4$ have also been isolated. Structures have been assigned to all the complexes on the basis of IR and NMR data.

IN view of the biological importance¹ of imidazole and its derivatives complexes of imidazoles with several first row transition metals as well as a few platinum group metals have been investigated in detail²⁻⁵; however similar complexes with rhodium have not received sufficient attention.

Gillard and coworkers⁶ studied some Rh(III) complexes of methylimidazole, while Cocever *et al.*⁷ reported the isolation of imidazole and N-methylimidazole complexes of Rh(I) containing 1,5-cyclooctadiene. Saillant and coworkers⁸ have prepared several complexes of rhodium with biimidazole, of the type $\text{Rh}(\text{COD})(\text{HBiIm})$, $[\text{Rh}(\text{COD})(\text{BiIm})_2]$, $[\text{Rh}(\text{CO})_2(\text{HBiIm})]$, $[\text{Rh}(\text{CO})_2(\text{BiIm})_2]$ (COD is 1,5-cyclooctadiene and H_2BiIm is biimidazole).

We have reported earlier⁹⁻¹⁰ the isolation of a series of cationic complexes of Rh(I) of the types $[\text{Rh}(\text{CO})_2(\text{N}-\text{N})]^+$, $[\text{Rh}(\text{CO})(\text{N}-\text{N})\text{L}_2]^+$ and $[\text{Rh}(\text{CO})(\text{Y})\text{L}_2]^+$ where N-N is 2,2'-bipyridyl or 1,10-phenanthroline, Y is a nitrogen heterocyclic ligand and L is a tertiary phosphine or arsine. We have extended these investigations to the isolation and study of a series of analogous complexes of rhodium containing imidazole, benzimidazole and substituted benzimidazoles.

Materials and Methods

The infrared (nujol mulls) and NMR (in CHCl_3 using TMS as internal reference) spectra were recorded on a Carl-Zeiss UR-10 spectrophotometer and Varian T-60 instruments respectively. Conductivity measurements were made using Toshniwal conductivity bridge type CL 01.02.

The complexes of the type $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$ were made as reported earlier⁹.

Carbonyl bis(triphenylphosphine)imidazole rhodium(I) perchlorate $[\text{Rh}(\text{CO})(\text{Izl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$ —To an ethanolic suspension of the complex $[\text{Rh}(\text{CO})_2(\text{Ph}_3\text{P})_3]\text{ClO}_4$, imidazole was added in the mole ratio 1:2. The mixture was refluxed on a steam-bath for about $\frac{1}{2}$ hr. The resulting yellow solution on evaporation under reduced pressure deposited the required compound as shining yellow crystals.

The corresponding compounds containing benzimidazole (Bzl), 2-methylbenzimidazole (2-MeBzl), 2-ethylbenzimidazole (2-EtBzl), 2-phenylbenzimidazole

(2-PhBzl) and 2-(β -pyridyl)benzimidazole (2- β -PyBzl) were prepared in the same way.

The triphenylarsine compounds with Bzl and 2- β -PyBzl were made starting from the complex $[\text{Rh}(\text{CO})_2(\text{Ph}_3\text{As})_3]\text{ClO}_4$.

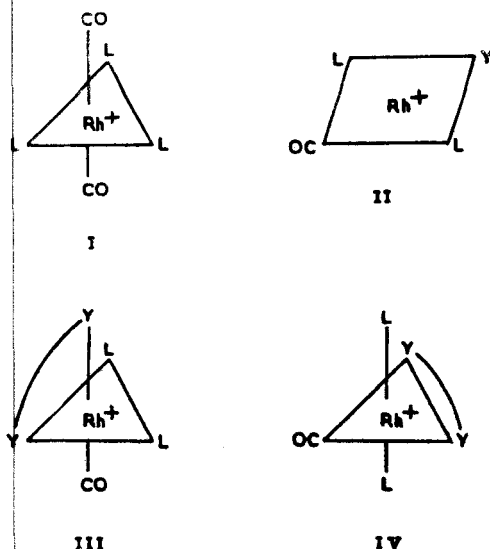
Carbonyl bis(triphenylphosphine)[2-(α -pyridyl)benzimidazole] rhodium(I) perchlorate $[\text{Rh}(\text{CO})(\text{Ph}_3\text{P})_2(2\text{-}\alpha\text{-PyBzl})]\text{ClO}_4$ —This compound was prepared as above using equimolar quantities of $[\text{Rh}(\text{CO})_2(\text{Ph}_3\text{P})_3]\text{ClO}_4$ and 2- α -PyBzl. The corresponding triphenylarsine, tri-*p*-tolylphosphine and tri-*o*-tolylphosphine complexes were also prepared in the same way.

Dicarbonyl[2-(α -pyridyl)benzimidazole]rhodium(I) perchlorate $[\text{Rh}(\text{CO})_2(2\text{-}\alpha\text{-PyBzl})]\text{ClO}_4$ —To a warm ethanolic solution of rhodium perchlorate saturated with carbon monoxide, 2-(α -pyridyl)benzimidazole in the mole ratio 1:1 was added and bubbling of carbon monoxide was continued when greenish-yellow crystals of the desired product got separated.

Dicarbonyl bis(2-phenylbenzimidazole)rhodium(I) perchlorate $[\text{Rh}(\text{CO})_2(2\text{-PhBzl})_2]\text{ClO}_4$ —This compound was also prepared in a similar way.

Results and Discussion

Cationic complexes of Rh(I) of the type $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$ (L is a tertiary phosphine or arsine) having configuration (I) react with imidazole, benzimidazole, 2-methylbenzimidazole, 2-ethylbenzimidazole and 2-phenylbenzimidazole to give four-coordinate cationic complexes of the type $[\text{Rh}(\text{CO})\text{YL}_2]\text{ClO}_4$ (Y = an imidazole type ligand). It has been shown that in compounds of this type the bond formation between the nitrogen donor ligand and metal takes place through the more basic pyridine nitrogen of the imidazole ring rather than through the pyrrole nitrogen¹. The ligand 2-(β -pyridyl)benzimidazole also gives a similar four coordinate complex but in this case it is rather difficult to say whether it is the nitrogen of the pyridyl ring or the nitrogen of the benzimidazole ring that coordinates to the metal. 2-(α -Pyridyl)benzimidazole (Y-Y), however acts, as a bidentate ligand in view of the favourable location of the nitrogen of the pyridine ring and gives five-coordinate complexes of the type $[\text{Rh}(\text{CO})(\text{Y}-\text{Y})\text{L}_2]^+\text{ClO}_4$ except in the case of the complex containing tri-*o*-tolylphosphine where a four-coordinate complex



$[\text{Rh}(\text{CO})(\text{Y}-\text{Y})\text{L}]\text{ClO}_4$ is formed presumably due to steric reasons¹⁰. All these complexes behave as 1:1 electrolytes in nitrobenzene, show a single νCO band around 2000, a broad νNH band around 3400 and a νClO_4 band around 1100 cm^{-1} in their IR spectra (Table 1).

The four-coordinate complexes should have a square planar geometry (configuration II) with the phosphine and arsine ligands occupying *trans*-positions. This is supported by the appearance of a single methyl resonance at τ 7.6 in the PMR spectrum of $[\text{Rh}(\text{CO})(2-\beta\text{-PyBzl})(p\text{-tolyl}_3\text{P})_2]\text{ClO}_4$. The five-coordinate complexes $[\text{Rh}(\text{CO})(2-\alpha\text{-PyBzl})\text{L}_2]\text{ClO}_4$ are formed by the displacement of one carbon monoxide and one phosphine (or arsine) from $[\text{Rh}(\text{CO})_2\text{L}_2]\text{ClO}_4$ (configuration I) and so probably have configuration (III) which is consistent with the tri-*p*-tolylphosphine containing complex showing a single methyl resonance in its PMR spectrum (though configuration IV also would be consistent with this result).

The basicity of the nitrogen donor ligands has been shown to increase slightly in the order $2-\beta\text{-PyBzl} < 2\text{-PhBzl} < \text{Bzl} < 2\text{-MeBzl} < 2\text{-EtBzl} < \text{Izl}$ ^{11,12}. We were expecting that this trend would be reflected in the electron density on the metal and hence in the νCO values of the corresponding complexes if the other ligand is kept constant. However, if one considers the complexes of these ligands containing triphenylphosphine, the νCO varies in the order $\text{Izl} > 2-\beta\text{-PyBzl} > \text{Bzl} > 2\text{-MeBzl} \sim 2\text{-EtBzl} > 2\text{-PhBzl}$ suggesting that no meaningful correlation can be made with the basicities of the ligands and νCO values of the complexes. Obviously other factors such as the π -acidity of the ligands which may not vary in the same sequence as the basicity also have to be considered.

One could also note the appreciable difference between the νCO value of a four-coordinate $2-(\beta\text{-pyridyl})\text{benzimidazole}$ containing cation and the νCO value of the corresponding five-coordinate $2-(\alpha\text{-pyridyl})\text{benzimidazole}$ containing cation. This is obviously due to the accumulation of higher electron density at the metal site in a five-coordinate complex due to the cumulative effect of the five σ -bonds that the ligands form with the metal and consequent transfer of greater electron density into the anti-bonding orbitals of carbon monoxide from the metal.

It is further found that the bidentate ligand $2-(\alpha\text{-pyridyl})\text{benzimidazole}$ reacts with rhodium perchlorate in alcoholic medium in the presence of carbon monoxide to give the four-coordinate cation $[\text{Rh}(\text{CO})_2(\text{Y}-\text{Y})]^+$. We could not isolate any solid compound under similar conditions using $2-(\beta\text{-pyridyl})\text{benzimidazole}$. However, $2\text{-phenylbenzimidazole}$ gives the complex ion $[\text{Rh}(\text{CO})_2(2\text{-PhBzl})_2]^+$. These two cations show two νCO bands in the 2000 cm^{-1} region indicating that the two CO molecules are *cis* to each other in both the complexes. In the phenylbenzimidazole containing complex, the

TABLE 1 — PHYSICAL PROPERTIES AND ANALYTICAL DATA OF CATIONIC COMPLEXES OF RHODIUM(I)

Compound ^a	m.p. (°C)	Λ^b	νCO (cm^{-1})	Analytical data (%) ^c		
				C	H	N
$[\text{Rh}(\text{CO})_2(2-\alpha\text{-PyBzl})]\text{ClO}_4$	>260	26.2	2047, 2107	37.3 (37.2)	1.8 (1.8)	9.2 (9.3)
$[\text{Rh}(\text{CO})_2(2\text{-PhBzl})_2]\text{ClO}_4$	242-45	24.4	2033, 2100	52.1 (52.0)	2.9 (3.1)	8.7 (8.7)
$[\text{Rh}(\text{CO})(\text{Izl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	189-92	28.1	2007	58.4 (58.4)	4.0 (4.2)	3.4 (3.4)
$[\text{Rh}(\text{CO})(\text{Bzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	215-16	25.0	1997	60.5 (60.5)	4.0 (4.2)	3.3 (3.2)
$[\text{Rh}(\text{CO})(2\text{-MeBzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	228-30	27.1	1987	61.0 (60.9)	4.2 (4.3)	2.3 (3.2)
$[\text{Rh}(\text{CO})(2\text{-EtBzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	229-30	27.7	1990	61.0 (61.3)	4.2 (4.5)	3.1 (3.1)
$[\text{Rh}(\text{CO})(2\text{-PhBzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	235	23.7	1980	63.2 (63.3)	4.1 (4.3)	2.9 (3.0)
$[\text{Rh}(\text{CO})(2-\beta\text{-PyBzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	240-43	21.3	2000	61.5 (62.0)	3.9 (4.0)	4.5 (4.4)
$[\text{Rh}(\text{CO})(2-\alpha\text{-PyBzl})(\text{Ph}_3\text{P})_2]\text{ClO}_4$	210-12	26.8	1940	61.6 (62.0)	3.8 (4.0)	4.4 (4.4)
$[\text{Rh}(\text{CO})(\text{Bzl})(\text{Ph}_3\text{As})_2]\text{ClO}_4$	228	26.0	1980	54.1 (54.9)	3.8 (3.8)	3.1 (2.9)
$[\text{Rh}(\text{CO})(2-\alpha\text{-PyBzl})(\text{Ph}_3\text{As})_2]\text{ClO}_4$	224-25	23.8	1947	57.1 (57.2)	4.9 (3.8)	4.4 (4.1)
$[\text{Rh}(\text{CO})(2-\beta\text{-PyBzl})(\text{Ph}_3\text{As})_2]\text{ClO}_4$	248	24.2	1980	56.5 (57.2)	3.8 (3.8)	4.1 (4.1)
$[\text{Rh}(\text{CO})(2-\beta\text{-PyBzl})(p\text{-tolyl}_3\text{P})_2]\text{ClO}_4$	227-29	23.8	2005	63.3 (64.0)	5.1 (4.9)	4.0 (4.1)
$[\text{Rh}(\text{CO})(2-\alpha\text{-PyBzl})(p\text{-tolyl}_3\text{P})_2]\text{ClO}_4$	203-05	23.3	1970	63.5 (64.0)	4.9 (4.9)	4.0 (4.1)
$[\text{Rh}(\text{CO})(2-\alpha\text{-PyBzl})(o\text{-tolyl}_3\text{P})]\text{ClO}_4$	236-38	24.0	1985	56.3 (56.0)	3.9 (4.0)	6.3 (5.8)

a, compounds are yellow or pale green in colour. b, molar conductance ($\text{ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$) of ca 10^{-3}M solutions in nitrobenzene (25°C). c, calculated values are in parentheses. d, τMe , 7.93. e, τMe , 7.60. f, τMe , 7.67.

cis configuration is obviously favoured because in the *trans* configuration the two CO molecules of high *trans* effect located *trans* to each other would mutually weaken the metal-carbon bonds and render the structure less stable.

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References

1. SUNDBERG, R. J. & BRUCE MARTIN, R., *Chem. Rev.*, **74** (1974), 471.
2. LANE, T. J., NAKAGAWA, I., WALTER, T. L. & KANDATHIL, A. J., *Inorg. Chem.*, **1** (1962), 267.
3. CHISWELL, B., LIONS, F. & MORRIS, B. S., *Inorg. Chem.*, **3** (1964), 110.
4. BOSE, K. S. & PATEL, C. C., *J. inorg. nucl. Chem.*, **33** (1971), 755.
5. CARMICHEL, J. W., CHAN, N., CORDES, A. W., FAIR, C. K. & JOHNSON, D. A., *Inorg. Chem.*, **11** (1972), 1117.
6. ADDISON, A. W., DAWSON, K., GILLARD, R. D., HEATON, B. T. & SHAW, H., *J. chem. Soc., Dalton*, (1972), 589.
7. COCEVAR, C., MESTRONI, G. & CAMUS, A., *J. organometal. Chem.*, **35** (1972), 389.
8. KAISER, S. W., SAILLANT, R. B. & RASMUSSEN, P. G., *J. Am. chem. Soc.*, **97** (1975), 425.
9. REDDY, G. K. N. & RAMESH, B. R., *J. organometal. Chem.*, **67** (1974), 443.
10. REDDY, G. K. N. & RAMESH, B. R., *J. organometal. Chem.*, **87** (1975), 347.
11. RABIGER, D. J. & JOULLIE, N. M., *J. Am. chem. Soc.*, **29** (1964), 476.
12. EFROS, L. S. & PORAI-KOSHITS, B. A., *Zur. obsh. Khim.*, **23** (1953), 697; *Chem. Abstr.*, **48** (1954), 7603a.