Cationic Carbonyl Complexes of Rh(I) with Imidazoles

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Cationic complexes of rhodium(I) of the type \([\text{Rh(CO)}_2\text{L}]\text{ClO}_4\) (L is PhaP or PhaAs) react with imidazoles to give four-coordinate complexes of the type \([\text{Rh(CO)}\text{Y-L}]\text{ClO}_4\) and five-coordinate complexes of the type \([\text{Rh(CO)}\text{Y-Y-L}]\text{ClO}_4\) [Y is imidazole, benzimidazole or substituted benzimidazole and (Y-Y) is 2-(\(\alpha\)-pyridyl)benzimidazole]. Complexes of the types \([\text{Rh(CO)}\text{Y-L}]\text{ClO}_4\) and \([\text{Rh(CO)}\text{Y-Y-L}]\text{ClO}_4\) 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 importance\(^4\) 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 detail\(^5,6\); however similar complexes with rhodium have not received sufficient attention.

Gillard and coworkers\(^6\) studied some Rh(III) complexes of methylimidazole, while Cooever et al.\(^7\) reported the isolation of imidazole and \(N\)-methylimidazole complexes of Rh(I) containing 1,5-cyclooctadiene. Saillant and coworkers\(^8\) have prepared several complexes of rhodium with imidazole, of the type \([\text{Rh(COD)}\text{HBilm}]\), \([\text{Rh(COD)}\text{BiIm})_2\], \([\text{Rh(COD)}\text{HBilm}]\), \([\text{Rh(COD)}\text{BiIm}]_2\) (COD is 1,5-cyclooctadiene and \(\text{HBilm}\) is benzimidazole).

We have reported earlier\(^9,10\) the isolation of a series of cationic complexes of Rh(I) of the types \([\text{Rh(CO)}_2\text{N-N}]\text{ClO}_4\), \([\text{Rh(CO)}\text{N-N-L}]\text{ClO}_4\) and \([\text{Rh(CO)}\text{N-N-L}]\text{ClO}_4\) where \(\text{N-N}\) 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 CDCl\(_3\) 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 \([\text{Rh(CO)}_2\text{L}]\text{ClO}_4\) were made as reported earlier\(^9\).

Catalonil \(L\text{is(triphenylphosphine)}\text{imidazol eradicate}(I)\) perchlorate \([\text{Rh(CO)}(\text{L})\text{PhaP}_2]\text{ClO}_4\) – To an ethanolic suspension of the complex \([\text{Rh(CO)}_2\text{PhaP}_2]_2\text{ClO}_4\), imidazole was added in the mole ratio 1:2. The mixture was refluxed on a steam-bath for about 1 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-(\(\beta\)-pyridyl)benzimidazole (2-\(\beta\)-PyBzl) were prepared in the same way.

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

Carbonyl bis(triphenylphosphine)(2-(\(\alpha\)-pyridyl)benzimidazole)rhodium(I) perchlorate \([\text{Rh(CO)}(\text{PhaP}_2)(2-\alpha\text{-PyBzl})\text{ClO}_4\]— This compound was prepared as above using equimolar quantities of \([\text{Rh(CO)}_2\text{PhaP}_2]\text{ClO}_4\) and 2-\(\alpha\)-PyBzl.

Dicarbonyl[2-(\(\alpha\)-pyridyl)benzimidazole]rhodium(I) perchlorate \([\text{Rh(CO)}_2(2-\alpha\text{-PyBzl})\text{ClO}_4\]— To a warm ethanolic solution of rhodium perchlorate saturated with carbon monoxide, 2-(\(\alpha\)-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(CO)}_2(2-\text{PhBzl})\text{ClO}_4\]— This compound was also prepared in a similar way.

Results and Discussion

Cationic complexes of Rh(I) of the type \([\text{Rh(CO)}_2\text{L}]\text{ClO}_4\) (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 complexes of the type \([\text{Rh(CO)}\text{L}]\text{ClO}_4\) (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 pyridine ring and gives five-coordinate complexes of the type \([\text{Rh(CO)}_2\text{L}]\text{ClO}_4\) (\(\text{L}\) is a nitrogen heterocyclic ligand) with the imidazole ring that coordinates to the metal.
The basicity of the nitrogen donor ligands has been shown to increase slightly in the order 2-~ PyBzl < 2-PhBzl < Bzl < 2-MeBzl < 2-EtBzl < Izl,12. We were expecting that this trend would be reflected in the electron density on the metal and hence in the vCO values of the corresponding complexes if the other ligand is kept constant. However, if one considers the complexes of these ligands containing triphenylphosphine, the vCO varies in the order Izl > 2-~ PyBzl > Bzl > 2-MeBzl > 2-EtBzl > 2-PhBzl suggesting that no meaningful correlation can be made with the basicities of the ligands and vCO values of the complexes. Obviously other factors such as the σ-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 vCO value of a four-coordinate 2-~-pyridylbenzimidazole containing cation and the vCO value of the corresponding five-coordinate 2-~-pyridylbenzimidazole 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-~-pyridylbenzimidazole reacts with rhodium perchlorate in alcoholic medium in the presence of carbon monoxide to give the four-coordinate cation [Rh(CO)(Y-Y)]+ of. We could not isolate any solid compound under similar conditions using 2-~-pyridylbenzimidazole. However, 2-phenylbenzimidazole gives the complex ion [Rh(CO)(2-PhBzl)2]+. These two cations show two vCO 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

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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