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WGSR catalyzed by *cis*-$[Rh(CO)_2(amine)_2]PF_6$ heterogenised on poly(4-vinylpyridine)

Alvaro J. Pardey[a,*], Marta Mediavilla[a], Massimo Canestrari[a], Caribay Urbina[a], Delfin Moronta[b], Eduardo Lujano[c], Pablo Baricelli[c,*], Clementina Longo[d], Rubén Pastene[e] and Sergio A. Moya[e,*]

[a] *Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*
E-mail: apardey@strix.ciens.ucv.ve
[b] *Escuela de Física, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*
[c] *Centro de Investigaciones Químicas, Facultad de Ingeniería, Universidad de Carabobo, Valencia, Venezuela*
[d] *Facultad de Farmacia, Universidad Central de Venezuela, Caracas, Venezuela*
[e] *Departamento de Química Aplicada, Facultad de Química y Biología, Universidad de Santiago de Chile,*
Santiago de Chile, Chile

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This paper describes catalytic activation studies of the water–gas shift reaction by *cis*-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, or 2,6-lutidine) heterogenised on poly(4-vinylpyridine) in aqueous 2-ethoxyethanol. The effect of varying the nature of the amine was investigated. The rhodium complexes bearing 4-picoline (4-pic) ligands proved to be most active among those surveyed, and displaying turnover frequencies for hydrogen production of 8.9 mol of H_2 per mole of Rh per day for 9.4×10^{-5} mol *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/1.00 g poly(4-vinylpyridine), $P(CO) = 0.9$ atm at 100 °C.

Keywords: water–gas shift reaction, rhodium, poly(4-vinylpyridine), carbon monoxide

1. Introduction

Catalysis of the water–gas shift reaction (WGSR)

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

by transition metal complexes both in solution [1–12] or heterogenised on polymers [13–19] has been reported.

Rhodium(I), *cis*-$[Rh(CO)_2(amine)_2]PF_6$, complexes dissolved in aqueous pyridine and substituted pyridines solution (amine = 4-picoline, 2-picoline, pyridine, or 2,6-lutidine) have been used as catalysts for the WGSR [3] as well as for the catalytic nitrobenzene reduction to aniline under WGSR conditions [20]. The catalytic activity was shown to be sensitive to the nature of amines. Both electronic and steric effects of the methyl groups apparently influence this trend.

Our current interest in the reduction of nitro derivatives [20,21] as well as in the catalysis of the WGSR by transition metal complexes [7,8,11,12] led us to study the catalytic properties of *cis*-$[Rh(CO)_2(amine)_2]PF_6$/poly (4-vinylpyridine) in aqueous 2-ethoxyethanol in order to compare the catalytic behavior of this polymer-supported system to its homogeneous counterpart formed by *cis*-[Rh $(CO)_2(pyridine)_2]PF_6$/pyridine and other substituted pyridines previously studied by Pardey and Ford [3] and restudied by Fachinetti et al. [5].

2. Experimental

2.1. Materials

Pyridine (py), 4-picoline, 3-picoline, 2-picoline (-pic) and 2,6-lutidine were obtained from Aldrich and distilled from KOH before use. $RhCl_3\cdot3H_2O$ was obtained from Aldrich. Water was doubly distilled. 2-ethoxyethanol (Aldrich) was distilled from anhydrous stannous chloride. Poly(4-vinylpyridine) (P(4-VP), 2% cross-linked was used as provided by Reilly Industries. The gas mixture CO/CH_4 (95.8%/4.2%, v/v) was purchased from BOC Gases. The rhodium complexes *cis*-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine or 2,6-lutidine) were prepared as reported by Pannetier et al. [22].

2.2. Catalyst preparation

A 1.00 g sample of P(4-VP) and a known amount of the rhodium complex *cis*-$[Rh(CO)_2(amine)_2]PF_6$ (ca. 1.0×10^{-4} mol) were stirred for 72 h in 10 ml of 2-ethoxyethanol until almost all the rhodium was extracted by the polymer from the solution as marked by the presence of a colorless clear solution above the polymer beads. The yellow polymer was filtered, washed with 2-ethoxyethanol (15 ml) to remove the unabsorbed rhodium complex of which the concentration was determined by UV-visible spectroscopy.

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[*] To whom correspondence should be addressed.

2.3. Catalyst testing

WGSR catalyst tests were performed under batch reaction conditions [3]. In a typical catalyst WGSR experiment, the supported rhodium species and 10 ml of aqueous 2-ethoxyethanol were added to the glass reactor vessel, then the solution was degassed by three freeze–pump cycles. The reaction vessel was charged with CO/CH_4 (95.8%/4.2%, v/v) mixture at the desired pressure, then suspended in a circulating thermostated (Cole–Palmer, model 71/Analog Controller) glycerol oil bath.

Gas samples of 1.0 ml were periodically removed from the reaction vessel at bath temperature with Pressure Lok syringes (Precision Sampling Corporation), analyzed by gas chromatography and corrected for small background signals. The CH_4 was present as an internal standard. The reaction vessel was flushed at the end of heating time (3 h) and then recharged with CO/CH_4 in a similar manner to that used for the initiation of the run. Darkening of the loaded polymer beads always occurred during the first 30 min of a WGSR run.

2.4. Instrumentation

UV-visible spectra were recorded on a Perkin–Elmer Lambda 10 spectrophotometer in 1.0 cm quartz cell. Infrared spectra were recorded on a Perkin–Elmer 1760X-FT spectrophotometer. The determinations of pH were performed on a Denver model Acumet Basic pH-meter. Gas sample analyses from catalytic runs were performed on a Hewlett–Packard 5890 series II programmable gas chromatograph fitted with Carbosieve-B (mesh 80–100) column and thermal conductivity detector. EPR experiments were carried out in a conventional Varian E-line X-band spectrometer, using a rectangular cavity operating in the TE 102 mode. The scanning electron micrographs were recorded on a Hitachi S-500 microscope with energy dispersive X-ray detector.

3. Results and discussion

3.1. Catalysis studies

The rhodium(I), *cis*-$[Rh(CO)_2(amine)_2]PF_6$, complexes heterogenised on P(4-VP) form systems which show catalytic activity in the WGSR at $P(CO) = 0.9$ atm, $T = 100\,°C$, in 10 ml of 80% aqueous 2-ethoxyethanol. For such systems, formation of H_2 and CO_2 was observed in the initial gas samples taken soon after the reaction solution reached operation temperature. Table 1 summarizes the production of hydrogen ($TF(H_2) = $ mol of H_2 (mol Rh × day)$^{-1}$) by the Rh heterogenised on P(4-VP). In each case a 1 : 1 H_2/CO_2 ratio was observed (within experimental uncertainties), as required by equation (1). No activity toward the WGSR was observed when the clear solution above the polymer beads was tested under similar experimental conditions but in the absence of the heterogenised amine rhodium complexes. The amount of the absorbed rhodium complex on P(4-VP) reported in table 1 was determined by subtracting the initial amount of rhodium complex (1.0×10^{-4} mol) from the unabsorbed one.

Table 1

Catalytic activity of *cis*-$[Rh(CO)_2(amine)_2]PF_6$ anchored on P(4-VP) in contact with aqueous 2-ethoxyethanol and *cis*-$[Rh(CO)_2(amine)_2]PF_6$ dissolved in aqueous pyridine and other substituted pyridines on the WGSR.[a]

Amine	[Rh][b] ($\times 10^{-5}$ mol)	pK_a[c]	TF(CO_2)[d]	TF(H_2)[d]
pyridine[a]	9.6	5.27	6.2	6.9
3-picoline[a]	9.4	5.52	7.4	7.4
2-picoline[a]	8.8	5.97	5.6	5.7
4-picoline[a]	9.4	6.00	8.9	8.5
2,6-lutidine[a]	8.4	6.75	3.9	3.7
4-picoline[a]	9.4	6.00	8.9	8.5
pyridine[e]	10.0	5.27	–	52
4-picoline[e]	10.0	6.00	–	80
2,6-lutidine[e]	10.0	6.75	–	1

[a] *cis*-$[Rh(CO)_2(amine)_2]PF_6$ anchored on 1.00 g of P(4-VP) in contact with 8 ml of 2-ethoxyethanol, 2 ml of H_2O, $P(CO) = 0.9$ atm at 100 °C.

[b] Amount of rhodium complex absorbed on P(4-VP) after 72 h.

[c] Reference [23].

[d] $TF(gas) = $ mol of gas (mol Rh × 24 h)$^{-1}$. Experimental uncertainty ca. ±10%.

[e] *cis*-$[Rh(CO)_2(amine)_2]PF_6$ dissolved in 10 ml of aqueous amine (2/8, v/v), $P(CO) = 0.9$ atm at 100 °C. From [3].

The results show that TF(H_2) values depend on the nature of the coordinated amine and decrease in the following order: 4-picoline $\geqslant$ 3-picoline $\geqslant$ pyridine > 2-picoline > 2,6-lutidine. A slight increase of WGSR activity with the increment of amine pK_a in absence of steric effect is observed. However, some differences were observed for the pyridines substituted in the *ortho* position; for example, the WGSR activity with the 2,6-lutidine ligand is the lowest due to the opposing steric effect of two *ortho* methyls. On the other hand, a more dramatic dependence of the TF values on the steric effects was found in the analogous homogeneous system; for example, 2,6-lutidine (1 day^{-1}) solutions proved to be roughly two orders of magnitude less active for the WGSR than those of 4-picoline (98 day^{-1}) [3].

WGSR activities determined in 80% aqueous 2-ethoxyethanol for these supported rhodium systems under 0.9 atm CO at 100 °C proved to be smaller than reported [3] for the catalyst prepared from *cis*-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline or pyridine) in aqueous 4-picoline or pyridine under similar conditions of [Rh], P(CO) and T. For example, the TF(H_2) of the supported Rh/4-picoline system (8.5 day^{-1}) is ten times lower than that for the homogeneous counterpart (80 day^{-1}). Catalytic activity decreases related to the use of polymer heterogenised catalysts have been previously observed [13]. However, catalytic activity of the *cis*-$[Rh(CO)_2(2\text{-pic})_2]PF_6$/P(4-VP) ($TF(H_2) = 5.7$ day^{-1}) supported system is two times higher than those of the homogeneous system formed by *cis*-$[Rh(CO)_2(2\text{-pic})_2]PF_6$/aq. 2-picoline ($TF(H_2) = 3$ day^{-1}).

Table 2
Recycling efficiency of WGSR catalyst by *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$/poly (4-vinylpyridine) in contact with aqueous 2-ethoxyethanol.[a]

Used time	TF(CO_2)[b]	TF(H_2)[b]
1st	8.9	8.5
2nd	8.7	8.5
3rd	8.7	8.5

[a] 1.00 g of P(4-VP), [Rh] (9.4×10^{-5} mol), 8 ml of 2-ethoxyethanol, 2 ml of H_2O, P(CO) = 0.9 atm at 100 °C for 5 h.

[b] TF(gas) = mol of gas (mol Rh × day)$^{-1}$. Experimental uncertainty ca. ±10%.

Probably due to the formation of different catalytic species of rhodium, both in solution and on P(4-VP).

In order to test the leaching and recycling efficiency of the anchored catalyst, the solution left after a catalytic run was analyzed by atomic absorption spectrophotometry and less than 0.01% of rhodium was detected in this solution. Also, the catalyst solid was reused two more times and its catalytic activity was checked on independent experiments under similar conditions. The results are given in table 2. No change of the catalytic activity was observed after repetitive use. On basis of the above results, it could be concluded that the polymer-anchored catalyst has a high stability and can be reused.

3.2. Spectroscopic studies

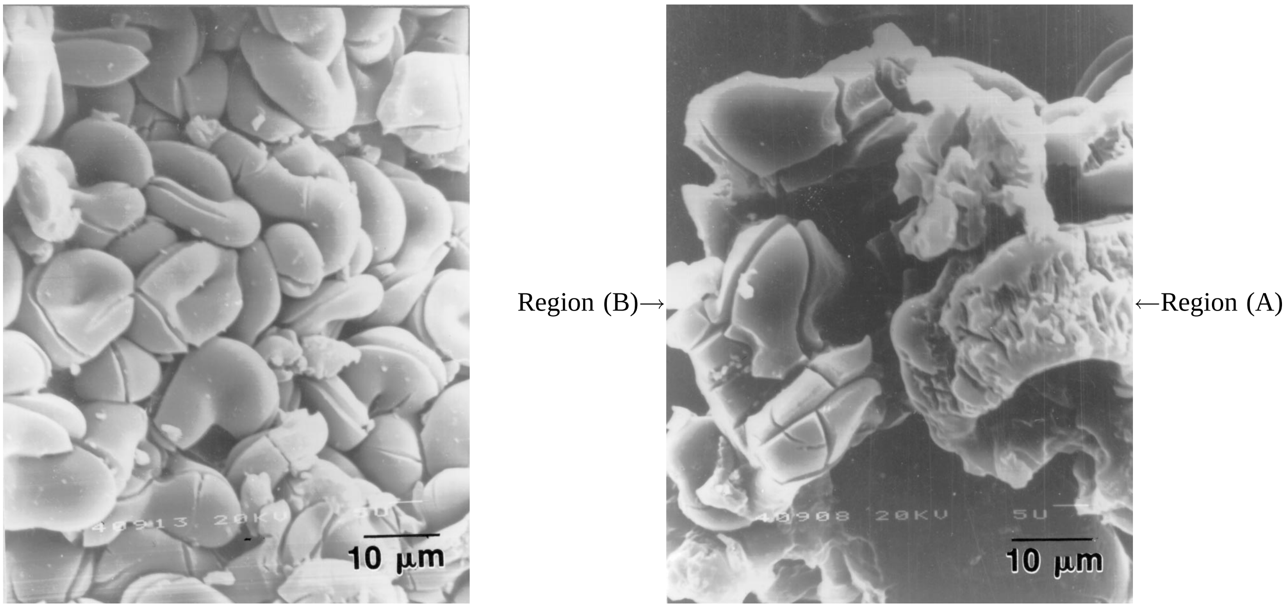
Attempts were made to assess the nature of the *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$/P(4-VP) catalyst by FT-IR, EPR spectroscopies, and scanning electron microscopy. The IR spectrum of a 250 mg sample of *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$ dissolved in 10 ml of 2-ethoxyethanol shows two strong bands in the ν_{CO} at 2083.6 and 2027.3 cm^{-1} for C_{2v} local symmetry. The IR spectrum of recently prepared KBr pellets of *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$ heterogenised on P(4-VP) shows no bands in the ν_{CO} region before being exposed to CO.

Scanning electron micrograph microscopy with energy dispersive X-ray (SEM-EDX) technique was used for the studies of the morphology and elemental composition of the solid samples. Figure 1(a) shows a SEM microphotograph of a P(4-VP) sample; it can be observed that the polymeric support is formed by agglomerates of grains with smooth surface. Figure 1(b) corresponds to the product of the reaction of P(4-VP) with *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$. The elemental analysis carried out in the etching areas (region A) allowed detection of Rh on them, while for the same type of analysis on the smooth regions, those without modifying their morphology (region B), Rh was not found in its composition. The modification of the surface in some areas of the polymeric support can be attributed to the heterogenisation of the rhodium complex on P(4-VP).

The IR and SEM-EDX results suggest that the nitrogen-functionalized polymer plays the role of a ligand and substitution of the two carbonyls does take place, as shown in equation (2):

$$\begin{aligned}\text{P(4-VP)} + \textit{cis}\text{-}\left[\text{Rh(CO)}_2\text{(4-pic)}_2\right]^+ &\rightarrow \\ \text{P(4-VP)–}\left[\text{Rh(4-pic)}_2\right]^+ &+ 2\text{CO}\end{aligned} \tag{2}$$

These results are similar to those of Kingston et al. [24] who observed that upon mixing pyridine with *cis*-[Rh(CO)$_2$Cl$_2$]$^-$ solution replacement of the two carbonyl groups occurs giving Rh(py)$_3$Cl$_3$. Also, Pardey and Ford [3] reported the reaction of *cis*-[Rh(CO)$_2$(py)$_2$]PF$_6$



(a) (b)

Figure 1. Scanning electron microphotograph of a P(4-VP) sample (a) and heterogenised *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$/P(4-VP) sample (b). Magnification 5000×.

with pyridine in N_2 atmosphere to give $[Rh(CO)(py)_3]PF_6$. In this case only one carbonyl is replaced.

The EPR spectrum of *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$ (5 mg) dissolved in 2 ml of 2-ethoxyethanol shows no paramagnetic signal as it was expected for diamagnetic compounds. A sample of P(4-VP) shows a very wide (4000 G) paramagnetic signal (figure 2(A)). A freshly heterogenised sample of *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/P(4-VP) before being exposed to CO shows a wide paramagnetic signal due to the polymer and a very clear four-fold hyperfine EPR signal due to rhodium nuclear $3/2$ spin (figure 2(B)).

The IR spectrum in KBr of the active Rh/4-pic heterogenised catalyst exposed to CO displays two bands at 1993.9 (carbonyl-linear Rh species) and 1833.1 cm^{-1} (carbonyl-bridged Rh species) suggesting the presence of rhodium carbonyl compounds on the surface of the polymeric support, but the detailed structure as well as the oxidation state(s) of the heterogenised carbonyl rhodium complexes are not clear yet. This postulate is based on an analogy with the reaction of rhodium sulfonated linear polystyrene with CO and H_2O [25], where different rhodium carbonyl species were identified. The two carbonyl bands disappeared when the solid catalyst was separated by filtration from the reaction solution and left for several days in air atmosphere. Analogous behavior has also been observed on an aminated polystyrene-bound rhodium cluster under similar conditions [15]. Also, the EPR signal intensity of the Rh/P(4-VP) sample exposed to CO (figure 2(C)) shows a notorious decrease. This indicates that CO coordination to rhodium changed the nature of active species and their oxidation state to non-paramagnetic species. This is also supported by the observation of Fachinetti et al., who reported [10] the reduction of mononuclear rhodium(I) *cis*-$[Rh(CO)_2(py)_2]^+$ to polynuclear rhodium(-I) $[Rh_5(CO)_{13}(py)_2]^-$ species by the CO/H_2O couple.

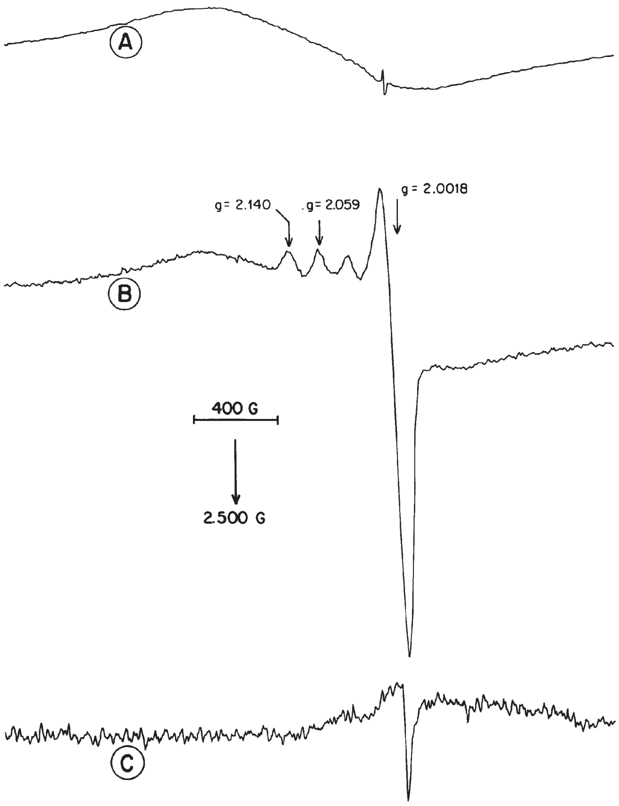


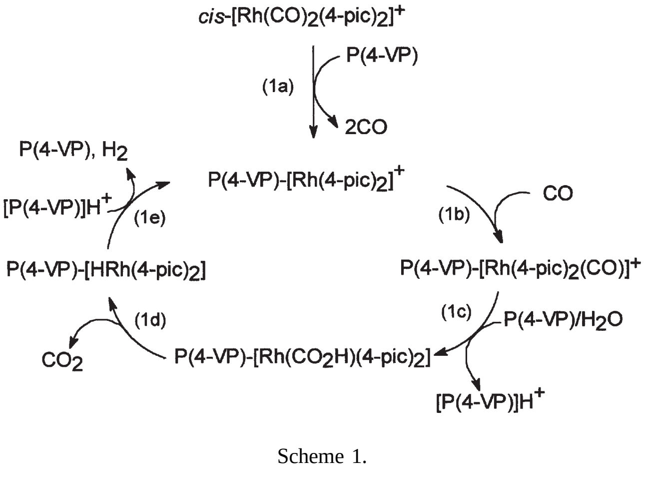
Figure 2. EPR spectra on the 1250–4000 G region of a P(4-VP) sample (A), a heterogenised *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/P(4-VP) sample (B), and of a heterogenised *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/P(4-VP) sample exposed to CO/H_2O (C).

A freshly prepared solution mixture of *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/P(4-VP) in 80% aqueous 2-ethoxyethanol gave a pH of 6.3, while an aged catalysis solution gave lower pH value 4.6. These observations and the IR results suggest that the polymer may be acting not only as a ligand for the rhodium center, but is likely to be acting both as a general acid and a general base in the catalysis cycle [19]. Also, Kirsch et al. reported [26] that pK_a of pyridine residues in P(4-VP) is 3.25 in aqueous ethanol (5.5/4.5, v/v).

3.3. Mechanistic considerations

The evaluation of the mechanism for WGSR catalysis by *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$ anchored on P(4-VP) in contact with aqueous 2-ethoxyethanol in CO atmosphere, shows some key features which should be noted: First, FT-IR spectroscopic studies of mature catalyst system point to the presence of mononuclear and polynuclear rhodium carbonyl anchored complexes. Second, the pH of the catalytic solution and the pK_a of pyridine residues suggest that the polymer is acting as a general acid and a general base in the catalysis cycle. Third, a similar mechanism has been proposed for the more active mononuclear species involved in homogeneous catalysis of the WGSR by *cis*-$[Ir(CO)_2(4\text{-pic})_2]PF_6$ aqueous 4-picoline system on the basis of spectroscopic and kinetic data [11]. Scheme 1 illustrates the proposed mechanism for WGSR catalysis by monomeric rhodium cationic species.

In scheme 1, the substitution of two CO (1a) by P(4-VP) insoluble ligand in the *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$ forms the P(4-VP)–$[Rh(4\text{-pic})_2]PF_6$ anchored complex. Carbonylation of the latter rhodium heterogenised complex leads to the formation of rhodium carbonyl complex (1b), as has



Scheme 1.

been discussed in section 3.2. Nucleophilic attack of H_2O assisted by the general base character of uncoordinated P(4-VP) on coordinated rhodium carbonyl ligand would give the rhodium hydroxycarbonyl anchored intermediate P(4-VP)–$[Rh(CO_2H)(4\text{-pic})_2]$ and the pyridinium moiety $[P(4\text{-VP})]H^+$ (1c).

Decarboxylation of rhodium hydroxycarbonyl intermediate would generate a rhodium hydride complex P(4-VP)–$[HRh(4\text{-pic})_2]$ (1d) and protonation of the latter by $[P(4\text{-VP})H]^+$ which acts as a general acid would give H_2, free P(4-VP), and P(4-VP)–$[Rh(4\text{-pic})_2]^+$ complex to get the catalytic cycle closed (1e).

4. Conclusions

It has been demonstrated that active WGSR catalysts are formed on heterogenised *cis*-$[Rh(CO)_2(amine)_2]PF_6$ complexes on P(4-VP) in aqueous 2-ethoxyethanol. Among the catalysts studied *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$/P(4-VP) was the most active. FT-IR, EPR, and SEM-EDX studies provide strong experimental evidence for the formation of carbonyl rhodium species as reaction intermediates under reaction conditions in which the P(4-VP) plays the role of an insoluble ligand which serves to immobilize the rhodium via coordination.

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