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HOMOGENEOUS CATALYSIS OF THE WATER–GAS SHIFT REACTION BY RHODIUM COMPLEXES IN AQUEOUS SUBSTITUTED PYRIDINE SOLUTIONS

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Summary

Described are quantitative studies of the water–gas shift reaction (WGSR) catalysis by homogeneous solutions of $RhCl_3$ in aqueous pyridine and other substituted pyridine solutions. This system is a stable, moderately active catalyst displaying turnover frequencies for hydrogen production ($TF(H_2)$) of about 10^2 moles H_2 per mole Rh per day for [Rh] = 0.01 mol l^{-1}, $P(CO) = 0.9$ atm and $T = 100$ °C with an E_a value of ~11.5 kcal mol^{-1} deg^{-1}. The $TF(H_2)$ values were first order in $P(CO)$ but displayed a complex dependence on [Rh]. The latter behavior can be explained in terms of the presence of mononuclear and dinuclear rhodium complexes in the catalysis solution, both active for the WGSR but the former being the more active. *In situ* IR and ^{13}C NMR spectroscopic studies confirm the presence of dimeric complexes with bridging carbonyls. These data are discussed in terms of potential catalysis cycles, and it is concluded that formation of dihydrogen is the probable rate-limiting step.

Introduction

The water–gas shift reaction (WGSR, eqn. 1) is a fundamental chemical process of key importance as a source of hydrogen from carbonaceous raw materials, as a method for adjusting CO/H_2 ratios in synthesis gas streams and in the reductions of nitrogen and sulfur oxides in exhaust gases.

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

The WGSR is also a sometimes undesirable side reaction in other catalytic processes involving the activation of carbon monoxide. Previous studies in

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these and other laboratories have demonstrated WGSR catalysis by a broad range of different transition metal complexes in homogeneous solution under remarkably varied conditions [1 - 7]. For example, virtually all simple metal carbonyls $M_x(CO)_y$ are WGSR catalysts in basic solution (alkaline or amines) and, while WGSR activity is less common in neutral or acidic solutions, a number of complexes have proved to be active under such conditions as well. Several rhodium catalysts have been reported as WGSR catalysts (or as precursors of active catalysts) under varied conditions including $[Rh(CO_2Cl]_2$ in an aqueous HCl/NaI/acetic acid solution [2], $Rh_6(CO)_{16}$ in alkaline ethoxyethanol [8] or different amine solutions [3, 9, 10], phosphine complexes in basic solutions [11] and several different polydentate aromatic nitrogen heterocycle complexes in neutral, basic or acidic solutions [12, 13].

In the course of exploring one of the latter such systems in these laboratories [14], it became a matter of interest to define more quantitatively a simple catalyst prepared from $RhCl_3$ in solutions of pyridine and its substituted derivatives. Notably, a similar catalyst was described in an early all-encompassing patent [15] published before much of the current interest in homogeneous WGSR was stimulated by independent discoveries [1 - 3] of reasonably well characterized molecular catalysts for this reaction. Described here is a detailed study of WGSR catalysis by a system prepared by dissolving $RhCl_3$ in aqueous solutions of 4-methylpyridine and other substituted pyridines.

Experimental section

Materials

The methyl pyridines (4-picoline, 3-picoline and 2-picoline) and dimethyl pyridines (2,6-lutidine and 3,5-lutidine) were obtained from Aldrich and were distilled from KOH before use. Pyridine was obtained from Mallinckrodt Co. and used without purification. All gases and gas mixtures CO, N_2, H_2, CO/CH_4 (94/6), CO/H_2 (80/20), $CO/CH_4/H_2/CO_2$ (85.05/4.94/4.88/5.13%) and He/H_2 (91.5/8.5) were purchased from Linde and were used as received. Water was doubly distilled. Rhodium trichloride was used as provided by Johnson-Matthey, Inc.

The rhodium complexes *cis*-$[Rh(CO)_2L_2]PF_6$ (L = 4-picoline, pyridine, 2-picoline or 2,6-lutidine) and *trans*-$[Rhpy_4Cl_2]Cl$ were prepared as reported [16, 17].

Instrumentation

UV–visible spectra were recorded on a Cary 118 spectrophotometer in 1.0 cm (Precision) or 0.1 cm (Hellma) quartz cells. The 1.0 cm cells were attached through graded quartz-to-pyrex seals and 'O' ring glass connectors to a Schlenck-type adaptor topped with a rubber septum so that reagents could be added anaerobically. Infrared spectra were recorded on a Perkin-Elmer 683 or a Digilab FTS-60 spectrophotometer using NaCl or IR Trans cells for solution samples and KBr pellets for solid samples. The ^1H and ^{13}C NMR spectra were recorded on a Nicolet 300 MHz FT–NMR spectrometer. The magnet was locked and shimmed to the deuterium signal of the solvent. Samples were dissolved in deuterated solvents which were used for locking and as internal references (residual protons).

Analysis of gas samples from catalysis runs were performed as described previously on a Hewlett-Packard 5830A programmable gas chromatograph, fitted with a thermal conductivity detector [18, 19]. The columns used were Carbosieve-B (mesh 80 - 100) obtained from Hewlett-Packard. The column temperature was programmed from 60 to 175 °C at a flow rate of 30 ml s^{-1} using a Linde prepared He/H_2 (91.5/8.5) mixture as the carrier gas. Mixtures of H_2, N_2, CO, CH_4 and CO_2 were separated and eluted in this order. Calibration curves were prepared periodically for CO, CO_2, CH_4 and H_2, the calibrations being linear for the first three but not for H_2. The validities of the calibrations were repeatedly checked by analyzing known gas mixtures, and individual analyses were found to be accurate and reproducible to better than 10%. In catalysis runs, the CH_4 was used as an internal standard to evaluate the extent of CO consumption.

Batch reactor procedures

Catalytic activity and kinetics runs were conducted in all-glass reactor vessels consisting of round bottom flasks (100 - 200 ml) connected via an 'O' ring sealed joint to a two-way Rotoflow® Teflon stopcock attached to the vacuum line [18, 19]. In a typical catalysis experiment, rhodium complex and solvent at room temperature were added to the reactor vessel, then the solution was degassed by two freeze–pump–thaw cycles. The reaction vessel was charged with a CO/CH_4 (94/6) mixture at the desired pressure, then suspended in a thermostatted paraffin oil bath.

During a run, gas samples were periodically removed from the reaction vessel at bath temperature by expansion into a small T-tube section of the vacuum line capped with a rubber septum through which a gas syringe could be inserted. The 1.0 ml samples were analyzed by gas chromatography using CH_4 as an internal standard and correcting for small background signals. This procedure allowed calculation of absolute quantities of CO consumed and of H_2 and CO_2 produced during a time interval. The reaction vessel was periodically flushed then recharged with the CO/CH_4 mixture in a manner similar to that used for the initiation of the run, except that the degassing step involved evacuating the reaction flask for a short time at room temperature to remove residual CO_2.

Results and discussion

Catalysis studies

The WGSR catalytic activity of $RhCl_3$ in aqueous pyridine was discovered in these laboratories while using such solutions as a control for

WGSR catalysis by aqueous solutions of the 2,7-bis(2′-pyridyl)-1,8-naphthyridine (bpnp) complex of rhodium(II), $[(bpnp)Rh_2(O_2CCH_3)_3]PF_6$ [14]. The latter compound and related species proved to be precursors of catalysts showing moderate WGSR activity in neutral, acidic or basic mixed organic solvent/water solutions and having reasonably good stability over a period of several weeks. The activities defined as turnover frequency (TF = moles of product, H_2 or CO_2/(g-atom. wt. of Rh)/(24 h) are summarized in Table 1, where it is notable that the most active system proved to be that in aqueous pyridine solution. However, since under closely analogous conditions, the control system of $RhCl_3 \cdot 3H_2O$ in 80% aqueous pyridine proved to display a catalytic activity greater than the rhodium bpnp complex, further studies were confined to this 'simpler' system.

Catalytic activities for the latter system under various conditions were determined using the batch reactor technique described in the Experimental section. Catalysis runs were carried out for 0.005 to 0.040 M [Rh] (typically 0.010 M) solutions prepared from $RhCl_3 \cdot 3H_2O$ with P(CO) ranging from 0.5 to 1.9 atm (typically 0.9 atm) in various aqueous/substituted pyridine solutions (typically 80/20 v/v 4-picoline/H_2O) over the temperature range 80 - 120 °C (typically 100 °C). For such a run, formation of H_2 was observed in initial gas samples taken soon after the reaction solutions reached operating temperature, and quantitative analysis of gases sampled indicated that H_2 production was matched by stoichiometrically equivalent CO consumption. For mature solutions, *i.e.* those which had been allowed to react for a period equal to several turnovers, CO_2 production was also found to be the stoichiometric equivalent of that for H_2, consistent with eqn. 1.

Figure 1 displays the formation of H_2 for catalysis runs in different solvents over a period of several days. It is notable that these plots show no sharp discontinuities and are essentially linear after the first points. These observations indicate that the turnover frequencies for H_2 production,

TABLE 1

WGSR activities by dinuclear rhodium naphthyridine complexes[a]

1	Complex	Solvent	TF(H_2)[g]
1	$[(pynp)Rh_2(O_2CCH_3)_2](PF_6)$[b]	THF/H_2O[d]	7
2	$[(bpnp)Rh_2(O_2CCH_3)_3]PF_6$[b]	THF/H_2O, HCl[e]	12
3	$[(bpnp)Rh_2(O_2CCH_3)_3]PF_6$[b]	dioxane/H_2O[d]	5
4	$[(bpnp)Rh_2(O_2CCH_3)_3]PF_6$[c]	pyridine/H_2O[f]	75

[a] P(CO) = 0.9 atm, 100 °C, pynp = 2(2′-pyridyl)-1,8-napthyridine bpnp = 2,7-bis(2′-pyridyl)-1,8-naphthyridine.

[b] [Rh] = 0.5 mM.

[c] [Rh] = 7.2 mM.

[d] 10 ml of solution; 8/2, (v/v).

[e] 10 ml of solution; 8/1/1, (v/v/v).

[f] 5 ml of solution; 4/1, (v/v).

[g] Mol H_2/mol complex/day. Experimental uncertainty is about ±10%.

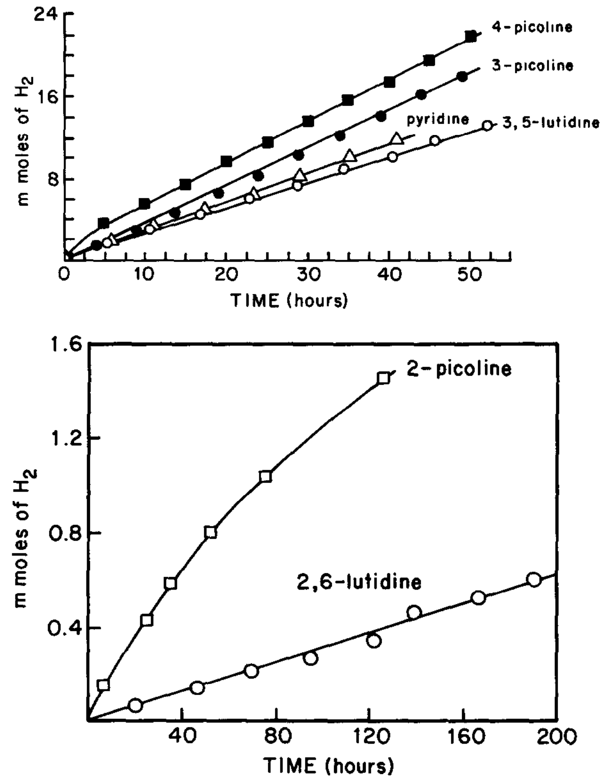


Fig. 1. Total H_2 produced as a function of time by a solution prepared from 0.1 mmol $RhCl_3 \cdot 3H_2O$ in 10 ml substituted pyridine/H_2O solutions (8/2, v/v) under 0.9 atm CO at 100 °C. Upper figure: reactions in sterically unhindered pyridines; lower figure: reactions in 2-methyl- and 2,6-dimethylpyridine.

TF(H_2), are essentially constant for the mature catalysts, a point which is emphasized by the plotted TF(H_2) and TF(CO_2) values for one such run in Fig. 2. Initial activities for H_2 production consistently exceeded those seen for the mature solutions by 20 - 30%. At 100 °C these catalysts were stable for observation periods up to several weeks in length. Unless otherwise noted, the TF values reported subsequently are for stable, mature solutions. These solutions have undergone some buffering owing to the CO_2 produced and the subsequent formation of carbonates. The shift in effective basicity was probed by diluting a sample of the solution tenfold with distilled water, then determining the resulting solution pH with a Radiometer model PHM84 pH meter. A freshly prepared solution of $RhCl_3$ in 80% aqueous 4-picoline gave a pH of 8.0 ± 0.1 when subjected to this treatment, while mature catalysis solutions, 0.005 - 0.020 M in rhodium, gave lower pH values 6.9 ± 0.1.

The TF values for this rhodium-based catalyst proved to be strongly dependent on the solvent medium. Table 2 summarizes the TF values measured for 0.01 M [Rh] in different solvents, each a 80/20 (v/v) substituted

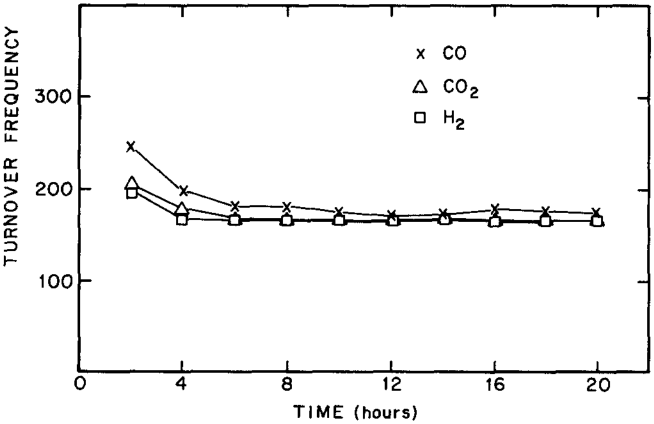


Fig. 2. Plots of turnover frequency (moles/mole Rh/days) *vs.* time for CO consumption (×), CO_2 production (△) and H_2 production (□) for WGSR catalysis at 110 °C under 0.9 atm CO by a 10 mM rhodium solution prepared from $RhCl_3$ in 80% aq 4-picoline.

TABLE 2

WGSR activities by $RhCl_3 \cdot 3H_2O$ in aqueous pyridine and substituted pyridines[a]

Amine	pKa[b]	$TF(H_2)$[c]
4-picoline	6.00	98
3-picoline	5.52	84
pyridine	5.27	68
3,5-lutidine	6.23	60
2-picoline	5.97	3
2,6-lutidine	6.75	1

[a] $P(CO)$ = 0.9 atm at 100 °C, [Rh] = 10 mM; 10 ml of solution amine/water, 8/2, v/v.
[b] From [24].
[c] Mol H_2/mol $RhCl_3 \cdot 3H_2O$/day. Experimental uncertainty is about ± 10%.

pyridine/H_2O mixture, in order to determine the dependence of these systems on the nature of the organic cosolvent. Modest differences were noted for those pyridines methylated in the *meta* or *para* positions with aqueous 4-picoline solutions displaying the highest activity. However, much more dramatic differences were observed for the solutions of pyridines substituted in the *ortho* position; for example 2,6-lutidine solutions proved to be roughly two orders of magnitude less active than those of 4-picoline. Among the sterically unhindered pyridine, there appears to be slight bias toward the more basic solvents, but the apparently opposing steric effect of one or two *ortho* methyls is dramatically larger. An equally dramatic dependence of the TF values was found for variation of the water component. In aqueous 4-picoline solutions, the approximately optimal activity was found for a 80/20 (v/v) 4-picoline/H_2O ratio (Fig. 3). It is this mixture which was used for the experiments described below. No formation of H_2 was observed

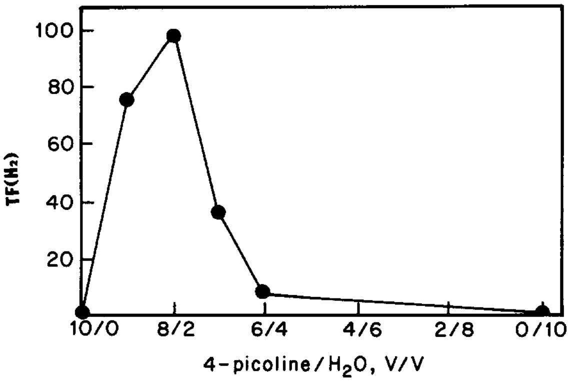


Fig. 3. Plot of TF(H_2) *vs.* the 4-picoline/H_2O ratio for catalysis by 10 mM rhodium solutions at 100 °C under 0.9 atm CO.

in neat 4-picoline, and TF values in solutions containing >40% H_2O were low.

For catalyst solutions prepared from $RhCl_3 \cdot 3H_2O$ in 80% aq. 4-picoline, the effects of varying the rhodium concentration, the CO pressure and the temperature are summarized in Tables 3 and 4 and Figs. 4 and 5. For all concentrations of rhodium (0.005 - 0.050 M) and temperatures (80 - 120 °C), a linear dependence of TF(H_2) (and correspondingly of TF(CO_2) and TF(CO)) upon *P*(CO) was noted (Fig. 4); however, an increase in [Rh] from 0.005 M to 0.020 M resulted in a decrease in TF(H_2), followed by nearly constant values at higher [Rh]. Arrhenius plots of the TF(H_2) values were clearly nonlinear for runs at lower [Rh], giving concave curves suggesting a lower E_a at temperatures below 100 °C (~8 kcal mol^{-1}) than at temperatures >100 °C (~14 kcal mol^{-1}). At the higher values of [Rh] the Arrhenius plots were roughly linear and gave an E_a value of about 11.5 kcal mol^{-1}.

WGSR runs were also initiated using the complexes *cis*-[$Rh(CO)_2L_2$]PF_6 (L = pyridine or 4-picoline) as the precursors to the catalysts. Activities determined in 80% aq. L solution under 0.9 atm CO and at 100 °C proved to be roughly 20% smaller in each case (TF(H_2) = 80 for 4-picoline, = 55 for pyridine) than reported for the catalysts prepared from $RhCl_3 \cdot 3H_2O$ in the same solvents (Table 2). Various explanations of this modest difference were considered, including the possibility that the composition of the $RhCl_3 \cdot 3H_2O$ might contain less water than indicated by the formula. However, a control WGSR run under the same conditions using a catalyst based on $RhCl_3 \cdot 3H_2O$ (0.1 mmol) in 10 ml of 80% (v/v) aqueous 4-picoline to which 0.1 mmol KPF_6 had been added was also ~20% less active than in the absence of KPF_6, suggesting some inhibition by PF_6^- anion or decomposition products. Notably, addition of up to 1.0 mmol NaCl to analogous catalysis solutions had no measureable effect on the TF(H_2) or TF(CO_2) values. It is also notable that the spectroscopic properties of the catalyst solutions prepared from $RhCl_3 \cdot 3H_2O$ or from *cis*-[$Rh(CO)_2L_2$]PF_6 did not appear to be significantly different (see below).

TABLE 3

Rhodium concentration effects on WGSR catalysis at constant CO pressure and at different temperatures[a]

$[RhCl_3]$ (mM)	T (°C)	$TF(H_2)$[b]
10	70	38
5	80	65
10	80	57
20	80	34
40	80	29
10	90	78
5	100	122
10	100	98
20	100	76
30	100	73
40	100	73
50	100	73
10	110	168
5	120	317
10	120	264
20	120	168
40	120	146
10	130	427

[a] $RhCl_3 \cdot 3H_2O$ in 10.0 ml of 4-pic/H_2O, 8/2 (v/v) under $P(CO) = 0.9$ atm.
[b] Mol H_2/mol Rh/day, experimental uncertainty is about ±10%.

TABLE 4

Carbon monoxide pressure effects on WGSR activities at constant rhodium concentration and different temperatures[a]

$P(CO)$ (atm)	T (°C)	$TF(H_2)$[b]
0.5	80	32
0.9	80	57
1.5	80	75
1.7	80	109
0.5	100	58
0.9	100	98
1.5	100	170
1.7	100	174
0.5	120	174
0.9	120	264
1.5	120	379

[a] 0.1 mmol $RhCl_3 \cdot H_2O$ in 10 ml of 4-picoline/H_2O, 8/2, (v/v).
[b] Mol H_2/mol Rh/day; experimental uncertainty is about ±10%.

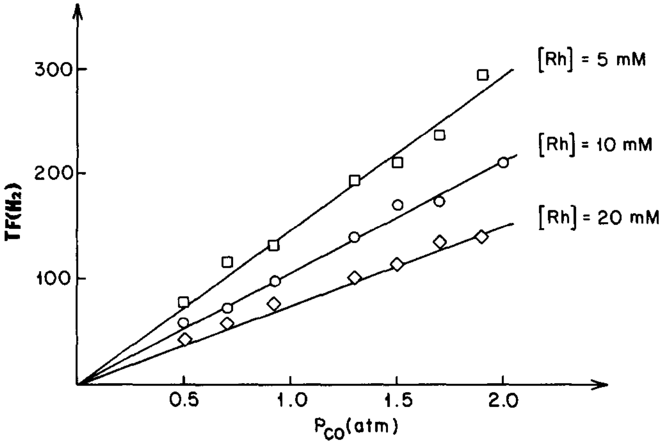


Fig. 4. Plots of TF(H_2) *vs.* *P*(CO) for different rhodium concentrations in 80% aqueous 4-picoline at 100 °C.

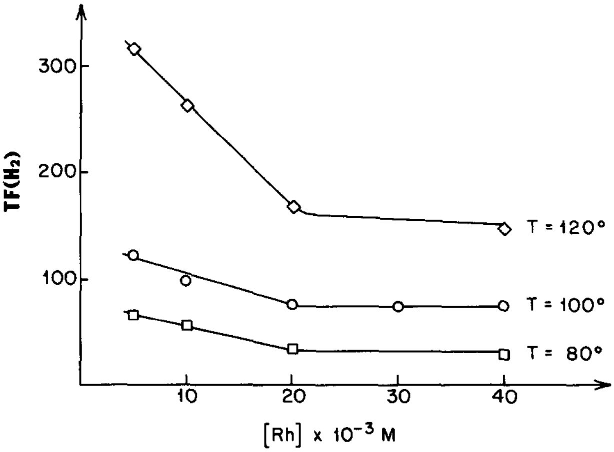


Fig. 5. Plots of TF(H_2) *vs.* [Rh] for different temperatures in 80% aq. 4-picoline under 0.9 atm CO.

Spectroscopic studies of catalyst and catalyst precursor solutions

Dissolution of $RhCl_3 \cdot 3H_2O$ (0.026 g, 0.10 mmol) in 10 ml of 80% aq. pyridine at room temperature leads to the gradual formation of an orange solution. After charging with CO (0.7 atm) and heating the reaction bulb in a 100 °C oil bath, this solution first changed to a yellow color, then (over 20 - 30 min) to an red-orange color, then, more rapidly, to the final dark brown color of a mature catalyst solution. Very similar color changes were seen when the solvent was 80% aqueous 3- or 4-picoline or 3,5-lutidine, but marked differences were seen with 2-picoline or 2,6-lutidine, which gave green rather than red-orange solutions in the intermediate stage after similar treatment. For the 80% aq. pyridine, 4-picoline or 3-picoline solvents, the electronic spectra of the red-orange solutions noted above each displayed a broad rising absorption from >500 nm with a well defined shoulder at approximately 400 nm (Table 5). The electronic spectra of the green solutions displayed a similar shoulder shifted ~10 nm to shorter wavelength, but also a weaker band at ~ 615 nm.

When the reaction of the aqueous pyridine solution under CO at 100 °C was quenched immediately after turning yellow by rapidly cooling and then the rhodium component isolated by removing the solvent under vacuum, the product consisted of bright yellow cyrstals with IR and UV/vis spectra identical to those for an authentic sample of *trans*-$[Rhpy_4Cl_2]Cl$ [17]. Similarly, the *trans*-$[RhL_4Cl_2]Cl$ product was isolated and identified for L = 4-picoline, and one may assume that the yellow solutions for L = 3-picoline or L = 3,5-lutidine represent formation of analogous precursors of the active catalysts. Heating a solution prepared from *trans*-$[RhL_4Cl_2]Cl$ in 80% aq. L under CO for about 20 min at 100 °C or allowing an analogous solution to react under CO (0.7 atm) at room temperature gave the red-orange solutions with electronic and IR spectra equivalent to those of the catalysis precursors (see below).

The formation of the orange-red solution was also observed when $RhCl_3 \cdot 3H_2O$ (0.053 g 0.20 mmol) in 10 ml 80% aq. substituted pyridine under CO (0.7 atm) was allowed to react for several days at room temperature. GC analysis of the gas phase above the product solution revealed CO_2 (0.16 mmol) as the sole gaseous product in roughly a 1/1 stoichiometric ratio to the amount of rhodium present, suggesting that the Rh(III) complex is reduced by CO to Rh(I) (eqn. 2). The IR spectrum of this solution

TABLE 5

Infrared and visible spectra data of solutions resulting from reactions of $RhCl_3$ in 80% aq. substituted pyridine solutions under CO[a]

Amine	Solution color	IR bands in the ν(CO) region[b] (cm^{-1})	Electronic absorption bands[c]
4-picoline	orange-red	2040(sh, s), 2010(sh, s), 1980(br, vs), 1820(vs) and 1760(s)	400 nm (sh, 1920)
3-picoline	orange-red	2048(sh, s), 2018(sh, s), 1985(br, vs), 1835(vs) and 1763(s)	400 nm (sh, 1880)
pyridine	orange-red	2040(sh, s), 2010(sh, s), 1980(br, vs), 1820(vs) and 1775(s)	399 nm (sh, 1150)
2-picoline	green	2050(sh, s), 1980(br, vs) and 1765(s)	618 nm (230), 384 nm (sh, 1570)
2,6-lutidine	green	2040(sh, s), 1985(br, vs) and 1765(s)	614 nm (90), 388 nm (sh, 1200)

[a] solvent = amine/water, 8/2, v/v, P(CO) = 0.7 atm, room temperature.
[b] sh = shoulder; br = broad.
[c] Values in parentheses are approximate extinction coefficient in M^{-1} cm^{-1}.

displayed five bands in the CO stretching region, three at frequencies characteristic of COs terminally coordinated to Rh(I), two at frequencies characteristic of bridging COs (Table 5).

$$\mathrm{Rh(III)} + \mathrm{CO} + H_2O \longrightarrow \mathrm{Rh(I)} + CO_2 + 2H^+ \qquad (2)$$

Formation of stoichiometric CO_2 was also observed for L = 4-, 3- or 2-picoline or 2,6-lutidine. However, while the spectral properties of the 3- and 4-picoline products were similar to those for L = pyridine, those for L = 2-picoline or 2,6-lutidine were considerably different (Table 5). In all cases, the key features of the IR spectra are the strong bands in the ν(CO) region, indicating the presence of both terminally and bridging coordinated carbonyls, hence the presence of dinuclear and/or polynuclear complexes.

The known Rh(I) carbonyl complexes *cis*-$[Rh(CO)_2L_2]PF_6$ (L = substituted pyridine) [20] were also used as precursors to the WGSR catalysts (see above). In $CHCl_3$ solution under N_2, the IR spectrum of *cis*-$[Rh(CO)_2py_2]PF_6$ displays two ν(CO) bands of nearly equal intensity at 2094 and 2018 cm^{-1}, and the electronic spectrum displays a single broad band centered at 344 nm ($\epsilon = 2.24 \times 10^3\ M^{-1}\ cm^{-1}$) which tails into the visible, giving the solution a yellow color. The same salt dissolved in pyridine or 80% aq. pyridine under CO gave (within 20 min at room temperature) a red-orange solution with spectral properties qualitatively identical to those seen for the solution formed from $RhCl_3 \cdot 3H_2O$ after several days at room temperature. Heating either solution to 100 °C for a few minutes gave the dark red-brown color characteristic of the mature catalyst solution, but after cooling to room temperature again, the IR spectrum was little changed with the exception of a weak band at 1853 cm^{-1}. Thus it appears that the major rhodium species present under these conditions was the same as in the red-orange precursor solution. Attempts to separate components of the catalysis solutions via column chromatography on alumina or silica proved unsuccessful.

Comparable results were obtained for L = 4-picoline. When a solid sample of *cis*-$[Rh(CO)_2(4\text{-pic})_2]PF_6$ (0.25 mmol) was dissolved at ambient temperature in 10 ml 80% aq. 4-picoline under a N_2 atmosphere, a golden solution was formed which displayed a single IR band in the carbonyl region located at 1985 cm^{-1}. GC analysis of the gas phase indicated the resulting formation of 0.32 ± 0.05 mmol of CO. Although the amount of CO formed appears high, these changes suggest the displacement of one CO, *e.g.*,

$$cis\text{-}Rh(CO)_2py_2^+ + py \longrightarrow Rh(CO)py_3^+ + CO \qquad (3)$$

(An analogous transformation was reported for the reaction of *cis*-$Rh(CO)_2py_2^+$ with PPh_3 in CH_2Cl_2 solution to give *cis*-$Rh(CO)(PPh_3)py_2^+$, $\nu(CO) = 1994\ cm^{-1}$ [20].) Introduction of CO to the system (in the form of a 94% CO, 6% CH_4 mixture, the CH_4 used as an internal calibrant) resulted in formation of the red-orange solution displaying five ν(CO) bands at 2040(s), 2010(s), 1980(vs), 1820(s) and 1760(s) cm^{-1}) in the IR spectrum. GC analysis of the gas phase indicated the consumption of 0.31 ± 0.05 mol of CO, thus the CO/Rh ratio of the species present must be 2.

The relative intensities of the five IR bands of the red-orange solution prepared from *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$ in 80% aqueous 4-picoline under CO at room temperature proved to be independent both of the rhodium concentration over the range 5 to 50 mM (Fig. 6) and of *P*(CO) over the range 0.1 to 1.0 atm. These results indicate that the five bands either belong to a single species present under the conditions or that, if two or more species are present, these must have the same order with respect to [Rh] and to [CO], *e.g.*, if the two species were isomers (see below). Since bridging carbonyls are apparent from the IR spectra, these results suggest that such complexes are polynuclear, perhaps dimers. Thus, while the band at 1980 cm^{-1} in these solutions has a frequency close to that of the single band seen in the absence of added CO, the similarities appear to be coincidental.

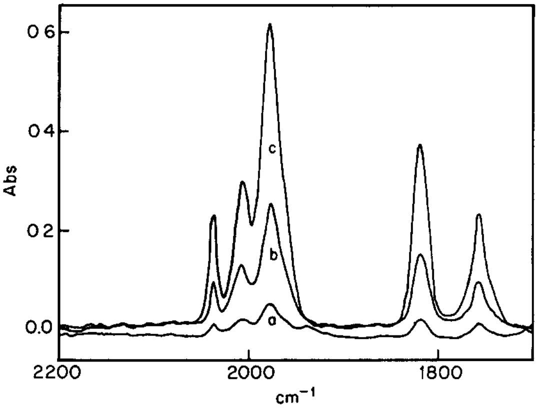


Fig. 6. IR spectrum (absorbance mode) of the carbonyl region for solutions prepared from *cis*-[Rh(CO)$_2$(4-pic)$_2$]PF$_6$ in 80% aq. 4-picoline under CO (1.0 atm). a, b and c represent rhodium concentrations of 5 mM, 20 mM and 50 mM, respectively.

The natural abundance ^{13}C NMR spectrum of *cis*-[Rh(CO)$_2$py$_2$]PF$_6$ in CDCl$_3$ under N$_2$ displayed a doublet centered at δ_c 188.2 ppm (*J*(Rh—C) = 71 Hz) which was assigned to the carbonyl carbons plus doublets at 151.2, 140.9 and 127.1 ppm with *J*(C—H) values 188, 154 and 170 Hz, respectively, assigned to the pyridine carbons. When a sample of this salt (0.115 g, 0.25 mmol) was dissolved in pyridine-d$_5$ under ^{13}CO (99%), the resulting red-orange solution gave a ^{13}C NMR spectrum at 25 °C with broad resonances in the CO region at 198.1, 188.4 and 183.1 ppm with possible very broad multiplets at approx. 208 and 224 ppm. When the temperature was lowered to −35 °C, four ^{103}Rh coupled carbonyl resonances were observed, triplets centered at δ_C 213.0 ppm (*J*(Rh—C) 27 Hz) and 224.8 ppm (35 Hz) and doublets centered at δ_C 183.2 ppm (62 Hz) and 198.2 ppm (*J*(Rh—C) 68 Hz), plus a broad singlet at 196.7 ppm, possibly due to the presence of free CO in solution (Fig. 7). The chemical shift and *J*(Rh—C) values for the triplets are consistent with those reported previously for carbonyls bridging two rhodium centers [21], while those for the doublets are consistent with

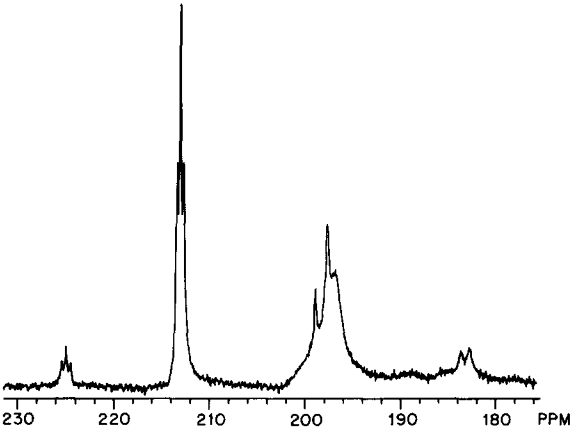


Fig. 7. ^{13}C NMR spectrum of the orange-red solution prepared from *cis*-[$Rh(CO)_2py_2$]PF_6 in pyridine-d_5 under ^{13}CO (1 atm). Spectrum recorded at −35 °C.

data for terminal COs on rhodium centers [22]. (For example the ^{13}C NMR spectrum of $Rh(CO)_2(CH_3CN)_2^+$ displays a doublet at 181.7 ppm with *J*(Rh—C) 73 Hz). The triplet at 213.0 ppm was substantially more intense than the one at 224.8 ppm, while the resonance at 198.2 ppm was the more intense doublet.

Observations of doublet ^{13}CO NMR resonances, indicating coupling to a single Rh, and triplet ^{13}CO resonances, indicating coupling to two Rh centers, confirm the above conclusions that the dominant species under these conditions must contain both bridging and terminally coordinated carbonyls. Such a species could be a dimer linked by one or, more likely, two bridging carbonyls, but the complexity of both the IR and ^{13}C spectra suggest the presence of two such dimers with the formulation [$Rh(CO)L_x$]$_2$(μ-$CO)_2^{2+}$ (see below). Notably, an early report [16] of the syntheses of the *cis*-[$Rh(CO)_2L_2$]PF_6 salts (L = pyridine or 4-picoline) suggested the formation of dimers bridged by carbonyls in the solid state, but this observation could not be confirmed in a later study [20]. Why dimers may form in aqueous pyridine solutions but not in the $CHCl_3$ solutions of *cis*-[$Rh(CO)_2L_2$]PF_6 is puzzling. One explanation might be that these are dimers of the 18 e^- adduct $Rh(CO)_2L_3^+$, the extra electron density on the metal centers favoring the formation of bridging carbonyls. However, this argument appears to be inconsistent with the apparent formation of dimers even for the sterically crowded 2-picoline and 2,6-lutidine.

When a similar red-orange solution prepared by dissolving *cis*-[$Rh(CO)_2$-py_2]PF_6 (0.02 mmol) in pyridine-d_5 (1.0 ml) under CO was then allowed to react with dihydrogen by flushing the solution with H_2, the color became much darker. The ^{1}H NMR of this solution at −30 °C showed three metal hydride resonances of approximately equal integrated intensities at δ_H − 13.9 (broad, −19.6 (triplet, *J*(Rh—H) 13.5 Hz) and −25.6 ppm (broad multiplet, possibly a triplet with *J*(Rh—H) ~ 9 Hz).

A sample of *cis*-(Rh(CO)$_2$py$_2$]PF$_6$ in pyridine-d$_5$ (2.5 ml) plus H_2O (0.6 ml) under ^{13}CO was heated to 100 °C for a few minutes to give the dark brown solution characteristic of the active WGSR catalyst. After this solution was cooled to −35 °C, the ^{13}C NMR spectrum in the carbonyl region displayed a rather busy spectrum of broad bands; however four of these fell into a positional and intensity pattern similar to that seen in Fig. 7. These occurred at 225.0 (weak), 215.5 (strong), 197 (broad, strong multiplet) and 184 (weak) ppm; however, additional weak resonances were also detected at 192(d), 206(d), 221(d), 237(m), 256(m) and 259(m) ppm. While the strongest bands of this spectrum at 215.5 and 197 ppm would (allowing for a modest solvent shift of the former) be consistent with the presence of the species which is dominant in the solution spectrum of Fig. 7, it is clear that the cooled catalyst solution also contains other, lesser carbonyl complexes. That one or more of these species might also be a rhodium hydride was indicated by ^{1}H NMR spectrum at 25 °C (run using pulse presaturation of the H_2O signal) which showed a weak hydride signal at $\delta_H - 25.3$ ppm.

Mechanistic considerations

In evaluating the mechanism for WGSR catalysis by the solutions prepared from $RhCl_3$ in 80% aq. 4-picoline or pyridine, the following observations are worthy of note:

(1) Spectroscopic studies (IR and C NMR) of mature catalyst solutions and model systems at ambient temperature and below point to the presence of polynuclear (probably dinuclear) rhodium complexes as the predominant species.

(2) Pyridines such as 2-picoline with methyl groups in the *ortho* position also form Rh(I) complexes with apparent bridging and terminal COs; however, the catalytic activity of these solutions are two orders of magnitude less than for the 4-picoline system.

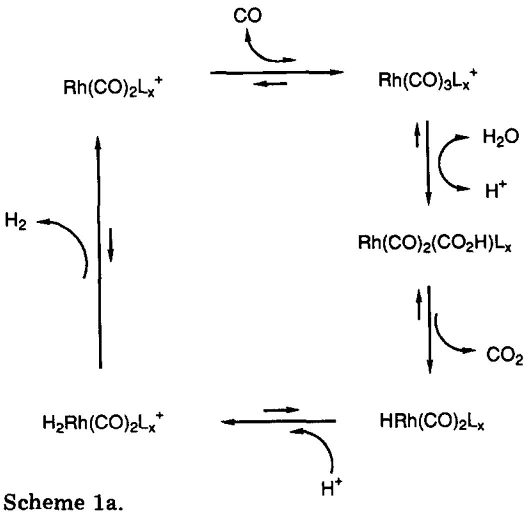
(3) Under catalysis conditions (80 - 120 °C) the dependence of the TF(H_2) values on [Rh] (Fig. 5) implies the participation of complexes having different nuclearities, *e.g.* mono- and dinuclear species (eqn. 4). That both types of species are catalytically active is indicated by TF(H_2) leveling to a constant value at higher [Rh]. The catalytic activity is first order in P(CO) and optimal in 80% aq. 4-picoline.

$$[\mathrm{Rh(CO)L}_x]_2(\mu\text{-CO})_2^{2+} \rightleftharpoons 2\mathrm{Rh(CO)}_2\mathrm{L}_x^{+} \qquad (4)$$

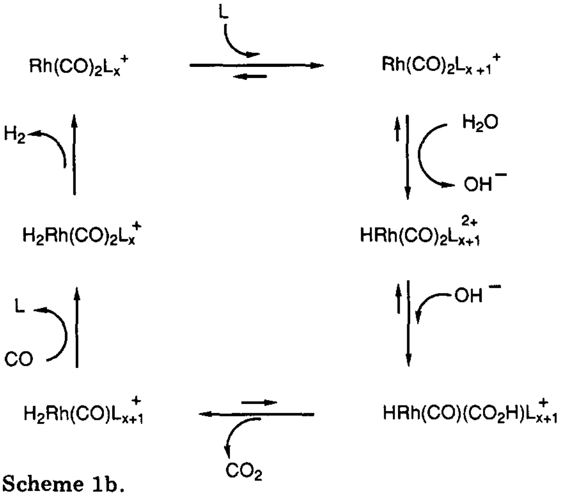
(where L = a substituted pyridine)

Scheme 1 illustrates two proposed mechanisms for WGSR catalysis by monomeric species. For each it is suggested that a key step may be the addition of a ligand, *i.e.* CO in Scheme 1a or L in Scheme 1b. Such an increase of the coordination number would be unfavorable for the bulky *ortho*-substituted pyridines, for which catalytic activity is much lower.

In Scheme 1a, the added CO would serve to enhance the electrophilicity of all the coordinated carbonyls, hence activate these toward attack



Scheme 1a.



Scheme 1b.

by the relatively weak nucleophile H_2O. If this were rate limiting, then the catalysis rate would be dependent on the concentration of the tricarbonyl species, hence display a first-order dependence on P(CO). The modest dependence of TF(H_2) on solvent basicity could then be explained by general base catalysis of the H_2O addition to the coordinated carbonyl. We have proposed a similar mechanism for the WGSR catalysis by ruthenium carbonyls in acidic aqueous diglyme solutions [23].

In Scheme 1b the proposed sequence of activation is reversed. Addition of another L to the coordination sphere would strongly enhance the basicity of the Rh(I) center. Protonation of this by H_2O would give, formally, a Rh(III) hydride complex plus hydroxide in solution. (Alternatively, oxidative addition of H_2O would give a Rh(III) hydroxy hydride complex.) Nucleophilic attack of OH^- or H_2O on a CO coordinated to this more electrophilic center would give, sequentially, the Rh(III) hydroxycarbonyl and dihydride species. The equilibrium to form the $H_2Rh(CO)_2L_x{}^+$ species prior to rate-limiting reductive elimination of H_2 would then rationalize first-order dependence of TF(H_2) on *P*(CO). A similar mechanism has been proposed for the less active WGSR catalysis by Rh(I) phosphine complexes, *e.g.*, $HRh[P(i\text{-}pr)_3]_3$, in aqueous pyridine solutions [11].

Two factors point to the latter mechanism as being the more likely. First, one would not expect as dramatic a dependence of the WGSR activity on the steric properties of the solvent if the ligand added were the smaller CO rather than the solvent itself. Second, the observation of a hydride signal in the mature solution NMR spectrum suggests that the rate-limiting step for the catalytic cycle is the H_2 elimination from a rhodium(III) center. However, neither observation provides a compelling reason for favoring Scheme 1b.

Analogous cycles may be proposed for the dinuclear complexes.

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