

Ru₃(CO)₁₂ in Acidic Media. Intermediates of the Acid-Cocatalyzed Water-Gas Shift Reaction (WGSR)

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The elucidation of the WGSR promoted by ruthenium carbonyls in acidic media started with the detection of the Ru(0), Ru(I), and Ru(II) intermediate complexes, namely Ru₃(CO)₁₂, Ru₂[μ-η²-OC(CF₃)O]₂(CO)₆, and *fac*-[Ru(CF₃-COO)₃(CO)₃][−], which accumulate when CF₃COOH is employed as an acid cocatalyst. Under catalytic conditions, the three were found to interconvert through elementary steps which produce CO₂ and H₂. In fact, Ru(0) is oxidized by H⁺ to Ru(I) and half the hydrogen of the catalytic cycle is supplied by this reaction. On the other hand, Ru(I) disproportionates to Ru(0) and Ru(II), and this latter species undergoes nucleophilic attack by H₂O. The decomposition of the metallacarboxylic acid intermediate gives back Ru(I), while H₂ and CO₂ are produced in a 1/2 molar ratio. The two alternating pathways for dihydrogen formation, namely Ru(0) oxidation by H⁺ and the decomposition of a metallacarboxylic acid intermediate, involve H₂ reductive elimination from the same RuHCF₃COO(CO)₂L₂ intermediate (L = H₂O, ethers). These findings define an acid-cocatalyzed WGSR whose distinctive features are (i) the intervention of a disproportionation reaction to generate a Ru(II) electron poor complex, whose CO ligands can undergo nucleophilic attack by water, (ii) the generation of the hydrido intermediate for dihydrogen production through two distinct reaction pathways, and (iii) the reductive elimination of H₂ from the hydrido intermediate without involving H⁺ from the medium.

Introduction

In acidic media Ru₃(CO)₁₂ is a catalyst precursor for homogeneous WGSR,¹ for the addition of carboxylic acids to alkynes,² and, under conditions of high temperature and pressure, for the production of ethylene glycol derivatives from syngas³ and for the syngas homologation of CH₃OH,⁴ esters,⁵ and carboxylic acids.⁶ On the other hand, the known fundamental chemistry of ruthenium carbonyls in acidic solutions is insufficient for the complete understanding of these catalytic reactions: all are believed to involve hydrido intermediates whose origin and nature were not demonstrated, however. Moreover, in the case of the here disclosed acid-cocatalyzed WGSR, not only the nature of the dihydrogen yielding hydrido complex but also the origin and the nature of the mandatory intermediates,⁷ bearing CO ligands susceptible of attack by water in acidic solutions, still remained obscure. On trying to characterize them, we met with some new aspects of the chemistry of ruthenium carbonyls, which are fundamental for a better understanding of catalytic reactions.

Experimental Section

General Methods. Unless otherwise specified, all operations were carried out under argon by standard Schlenk techniques. CO (<0.1% H₂) was purchased from Matheson, and AR grade toluene, py, iso-PrOH, THF, THF-*d*₈, diglyme, CF₃COOH, CF₃COOCs, CF₃SO₃H, and

NaBPh₄ from Aldrich. The ethers were further purified by distilling them from LiAlH₄, with THF and THF-*d*₈ under an Ar atmosphere and diglyme under vacuum; CF₃COOCs was anhydried under vacuum at 120 °C. Ruthenium trichloride hydrate was used as received from Chimet SpA. The ruthenium complex Ru₃(CO)₁₂ was prepared by literature methods.⁸ The IR spectra were recorded on a Perkin-Elmer Model FT-IR 1725-X, and ¹H and ¹⁹F NMR spectra on a Varian Model Gemini-200. Liquid samples for infrared spectra were taken off with a syringe and transferred to a 0.1 mm CaF₂ cell. Analyses of H₂ in gas samples from catalysis run were performed by a DANI Model 3200 gas chromatograph equipped with HW detector and a molecular sieve column with Ar as carrier gas. A calibration curve was prepared periodically. CO₂ was determined by bubbling the reaction gases through 25 mL aliquots of a 0.098 N Ba(OH)₂ solution and back-titration (phenolphthalein end point) of Ba(OH)₂ excess. The apparatus and procedures for the gas volumetric measurements were those described in the literature.⁹

Batch Reactor Procedures. Catalytic activity runs were carried out at 95 °C, P_{CO} = 0.8 atm in an all glass vessel with a volume of 316 mL, similar to that described in the literature.¹⁰ During a typical run, gas samples (1 mL) were removed at 1.5-h intervals and analyzed by GC.

Ru₂[μ-η²-OC(CF₃)O]₂(CO)₆ (1a). Ru₃(CO)₁₂ (5.0 g, 7.82 mmol) was suspended in diglyme containing 8 M H₂O and 0.8 M CF₃COOH (total volume = 100 mL) and heated to 100 °C during 12 h. The resulting orange solution was concentrated under vacuum (20 mmHg, 100 °C) leaving a deep red oil which was treated with toluene (200 mL). This homogeneous solution was stirred under CO atmosphere at 40 °C during 2 h and then stored 24 h at −20 °C. A 5.9 g amount of pale yellow crystals of **1a** (85% yield) was obtained and gave satisfactory analytical data. FT-IR (Nujol mull): ν_{CO} 2102 vs, 2051 vs, 2017 vs, 1993 s, and 1665 s cm^{−1}.¹¹

Ru₂[μ-η²-OC(CF₃)O]₂(CO)₄L₂ (L = H₂O, Diglyme) (1b). A 0.350 g amount of **1a** was dissolved in diglyme containing 8 M H₂O (total

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Table 1. Crystal Data and Details of Structure Refinements

empirical formula	C ₉ CsF ₉ O ₉ Ru	C ₁₀ H ₈ F ₆ O ₈ Ru	C ₄₁ H ₃₆ BN ₃ O ₂ Ru
fw	657.07	471.23	714.61
temp, K	293(2)	293(2)	293(2)
wavelength, Å	0.71073	0.71073	1.54178
cryst system	monoclinic	monoclinic	hexagonal
space group	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	P6 ₅ (No. 170)
a, Å	8.3839(5)	12.486(2)	9.7604(6)
b, Å	14.450(3)	10.228(2)	9.7604(9)
c, Å	16.079(1)	12.286(2)	64.244(8)
α, deg	90	90	90
β, deg	102.951(5)	107.76(2)	90
γ, deg	90	90	120
V, Å ³	1898.4(4)	1494.2(5)	5300.3(9)
Z	4	4	6
D(calc), Mg/m ³	2.299	2.095	1.343
abs coeff, mm ⁻¹	2.840	1.159	3.892
F(000)	1224	920	2208
cryst size, mm	0.34 × 0.24 × 0.22	0.25 × 0.25 × 0.08	0.21 × 0.21 × 0.48
θ range for data colln, deg	1.92–24.99	2.63–20.99	5.23–59.85
h ranges	–1 to 9	–12 to 12	–8 to 0
k ranges	–1 to 17	–10 to 1	0 to 10
l ranges	–19 to 18	–1 to 12	–72 to 64
reflcs collcd	4312	2134	5129
indepdt reflcs	3248 [R _{int} = 0.022]	1596 [R _{int} = 0.057]	5129
refinement method	full-matrix least squares on F ²	full-matrix least squares on F ²	full-matrix least squares on F ²
data/restraints/params	3240/30/239	1596/16/150	5129/5/436
goodness-of-fit on F ²	1.029	1.069	1.108
final R indices [I > 2σ(I)]	R ₁ = 0.0526, wR ₂ = 0.1278	R ₁ = 0.0890, wR ₂ = 0.2200	R ₁ = 0.0343, wR ₂ = 0.0764
R indices (all data)	R ₁ = 0.0727, wR ₂ = 0.1863	R ₁ = 0.1633, wR ₂ = 0.2865	R ₁ = 0.0735, wR ₂ = 0.0886
largest diff peak and hole, e ⁻ Å ⁻³	1.110 and –0.794	1.212 and –0.981	0.841 and –1.178

volume = 20 mL), and the solution was briefly evacuated. Under an inert atmosphere the IR spectrum consisted of the absorptions of **1b** at 2043 s, 1989 m, and 1958 vs cm⁻¹.¹¹ By restoration of a CO atmosphere, gas absorption took place and absorptions of **1a**, together with those of **1b** became evident.

[fac-Ru(OCOCF₃)₃(CO)₃]Cs (2). A catalytic run was carried out by employing Ru₃(CO)₁₂ (0.250 g, 0.39 mmol) in diglyme containing 8 M H₂O, 3 M CF₃COOH, and 0.4 M CF₃COOCs (total volume = 20 mL). The run was protracted overnight and then stopped by lowering the temperature to 20 °C. Colorless crystals of **2** (0.310 g, 40% yield), suitable for an X-ray investigation, separated out within 1 day. Satisfactory analytical data were obtained. FT-IR (Nujol mull): ν_{CO} 2145 s, 2084 vs 2067 vs, and 1693 s cm⁻¹. The molecular structure is reported in Figure 2.

Disproportionation Reaction of 1a. **1a** (0.650 g, 1.09 mmol) and CF₃COOCs (0.270 g, 1.09 mmol) were dissolved in 20 mL of anhydrous THF and placed under a CO atmosphere at 30 °C. Within 8 h, 1.07 mmol of gas was absorbed while orange Ru₃(CO)₁₂ separated out (0.220 g, 0.34 mmol, 95% yield; ν_{CO} (*n*-hexane) 2061 s, 2031 s, and 2013 m cm⁻¹). On evaporation of the mother liquor to dryness under vacuum, a pale yellow residue of **2** was obtained (0.710 g, 1.08 mmol, 99% yield; ν_{CO} (Nujol): 2145 s, 2084 vs, 2067 vs, and 1693 s cm⁻¹).

Reaction between 2 and H₂O. (a) **At 95 °C, in the Presence of CF₃COOH.** A 20 mL aliquot of a 8 M H₂O, 0.5 M CF₃COOH, and 0.036 M **2** (0.470 g, 0.71 mmol) solution in diglyme was placed under an Ar atmosphere in the 316 mL reaction vessel used for the catalytic runs. By the increase of the temperature up to 95 °C, the colorless solution turns yellow. After 1 hour the H₂ (0.35 mmol, 99% yield) and the CO₂ (0.69 mmol, 97% yield) were quantitatively determined. The IR spectrum of the liquid phase showed only the absorptions of **1b**. ν_{CO}: 2043 s, 1989 m, 1958 s cm⁻¹.

(b) **At Room Temperature.** **2** (0.443 g, 0.67 mmol) was dissolved in diglyme containing 8 M H₂O (total volume = 20 mL) under an Ar atmosphere in the 316 mL reaction vessel used for the catalytic runs. A pale yellow color was immediately observed, and the reaction was monitored by IR spectroscopy. After 45 min at room temperature, only the IR absorptions of a **3a–c** mixture of hydrido complexes became detectable (ν_{CO}: 2041 and 1957 cm⁻¹). Only trace amounts of H₂ were detected in the gas phase, while quantitative determination of the produced CO₂ gave 0.62 mmol (92% yield).

Dihydrogen Formation from a 3a–c Mixture of Hydrides. **4** (0.470 g, 1 mmol) was reacted at room temperature with 8 M H₂O in

diglyme (total volume = 20 mL) in the vessel for catalytic runs. After 45 min CO₂ formation ceased; the atmosphere was replaced by pure argon and the temperature raised to 65 °C. Gas samples (1 mL) were periodically taken off, and H₂ was determined by GC (Figure 6). After 24 h the IR spectrum of the liquid phase showed only the absorptions of **1b** (ν_{CO}: 2043 s, 1989 m, 1958 s cm⁻¹). An identical solution ([Ru] = 0.05 M, [H₂O] = 8 M in diglyme, total volume = 20 mL) in the same 316 mL reaction vessel was treated with 130 μL (1.5 mmol) of CF₃SO₃H at the end of CO₂ formation and then warmed to 65 °C. The H₂ formed at various times was determined as before.

{fac-Ru(OCOCF₃)₂(CO)₃[(CH₃)₂CHOH]} (4). Ru₃(CO)₁₂ (5.0 g, 7.82 mmol) was suspended in diglyme containing 8 M H₂O and 2.2 M CF₃COOH (total volume = 50 mL) and warmed to 100 °C during 12 h. The resulting orange solution of **1a** was stirred under a P_{CO} = 1 atm at room temperature for 5 days. As a consequence of the disproportionation reaction, Ru₃(CO)₁₂ separated out and was removed by filtration. The mother liquor was evaporated to dryness under vacuum at 100 °C, leaving an orange oil which was dissolved in 15 mL of *iso*-PrOH. A 200 mL volume of toluene was then added and the solution concentrated under vacuum at room temperature, till the precipitation of colorless crystals of **4** occurred (3.43 g, 7.28 mmol, 31% yield; ν_{CO} (Nujol) 2153 s, 2094 vs, 2078 vs, and 1676 s, broad, cm⁻¹). Satisfactory analytical data were obtained. The molecular structure is shown in Figure 3.

¹H NMR Spectra. **2** (0.130 g, 0.20 mmol) was dissolved in THF-*d*₈ containing 8 M H₂O (total volume 0.5 mL) and allowed to stand for 1 h. The spectrum of Figure 4a was then obtained. **4** (0.095 g, 0.20 mmol) was dissolved in THF-*d*₈ containing 8 M H₂O (total volume 0.5 mL) and allowed to stand for 1 h. The spectrum of Figure 4b was obtained and was converted into that of Figure 4a by addition of 0.052 g (0.21 mmol) of solid CF₃COOCs, directly in the NMR tube. In another experiment **4** was reacted with 8 M H₂O in THF-*d*₈ at the same concentration as before. By means of a syringe, increasing amounts of CF₃SO₃H were then added directly into the NMR tube. The spectra of Figure 4c–f were obtained at CF₃SO₃H/Ru = 0.42, 0.72, 1.36, and 2.40 molar ratios, respectively.

[fac-RuH(CO)₂(py)₃][BPh₄] (5). **4** (1.32 g, 2.8 mmol) was dissolved in 25 mL of THF, and 5 mL of H₂O was added at room temperature. After 1 h, 1.3 g (3.8 mmol) of NaBPh₄ in 20 mL of py was added, and the product was precipitated by addition of 150 mL of CH₃OH. After 1 week at 4 °C 1.7 g (2.38 mmol, 85% yield) of **5**¹⁷ was collected as colorless crystals. The molecular structure is reported in Figure 5.

X-ray Structure Determinations. The crystals of $[fac\text{-Ru}(\text{OCOCF}_3)_3(\text{CO})_3]\text{Cs}$ are colorless monoclinic prisms defined by the form $\{011\}$ closed by the pinacoid $\{100\}$. One of them was glued at the end of a glass fiber and was mounted on a Siemens P4 automatic single-crystal diffractometer, equipped with a graphite-monochromatized Mo K α radiation. Cell parameters were calculated on the accurately centered setting angles of 25 strong reflections with $12.5^\circ \leq \theta \leq 13^\circ$. Details about the crystal parameters and intensity data collection are summarized in the second column of Table 1. The Laue class was established by an automatic procedure contained in the diffractometer control program.¹² A redundant set of data was collected to estimate the collection accuracy. Three standard reflections measured every 97 measurements showed no decay in the crystal. The space group was univocally established as $P2_1/c$ on the basis of systematic absences. The collected intensities were corrected for Lorentz and polarization effects and for absorption by a Gaussian integration method.¹³ The equivalent reflections present in the set were then merged resulting in an internal R value ($R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum (F_o^2)$) of 0.022. The structure was solved by the automatic Patterson method contained in the SHELXTL² program, and the molecule was completed by means of the next Fourier map. Disorder in the positions of the CF₃ groups was suggested by electron density maps. The disorder was explained as a statistical distribution of the trifluoroacetate groups on two different conformations, and two different CF₃ groups were introduced in each position imposing the sums of occupancies equal to 1.

The final refinement cycles were made with anisotropic thermal factors for Cs, Ru, O, and C atoms and isotropic for F atoms and imposing geometrical constraints to the CF₃ modifications. The final reliability factors are showed in Table 1, where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [w(F_o^2 - F_c^2)^2 / w(F_o^2)^2]^{1/2}$, and $w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 12.34P]$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3$ and $S = [w(F_o^2 - F_c^2)^2 / (N - P)]^{1/2}$.

The crystals of $\{fac\text{-Ru}(\text{OCOCF}_3)_2(\text{CO})_3[(\text{CH}_3)_2\text{CHOH}]\}$ (**4**) are colorless milky, with a prismatic shape. Some of them were sealed within glass capillaries under a nitrogen atmosphere and were examined on a Siemens P4 single-crystal diffractometer. All the samples appeared to be crystalline, but not one presented a good diffraction profile. In fact some profiles appeared to be exceedingly large and some other showed a depression in the central part of the profile as they corresponded to two different single crystals slightly misaligned. The third column of Table 1 summarizes the relevant crystal data and intensity data collection details. Cell parameters were calculated from the setting angles of 13 accurately centered strong reflections having $8.9^\circ \leq \theta \leq 9.6^\circ$. The choice of such a low value for $\max$, here and in the intensities collection, has been called for by the lack of intense diffractions at high angles.

A redundant set of data was collected to verify, on merging, the collection reliability. Three standard reflections measured every 97 measurements allowed one to exclude any crystal decay. The collected data were corrected for Lorentz and polarization effects, but not for absorption, since a scanning around the ψ angle of 5 intense reflections showed a slight effect on the measured intensity.

The space group was univocally established as $P2_1/c$ by systematic extinctions, and the structure was solved by direct methods contained in the TREF¹³ procedure. However, the two CF₃ groups of the trifluoroacetate ligands and two methyl groups of isopropyl alcohol could not be reliably localized in a rather smeared electron density that appeared on the Fourier map. We explained this fact with the presence of disorder both in $-\text{CF}_3$ and in $-\text{CH}(\text{CH}_3)_2$ groups. As in the case of the cesium salt, we have introduced two distinct idealized $-\text{CF}_3$ groups in each expected position of trifluoroacetate ligand and two different $-\text{CH}(\text{CH}_3)_2$ groups in the isopropyl alcohol, assuming a total occupancy equal to 1 for each group. The atoms found in the Fourier map were refined with anisotropic thermal factors, while isotropic factors have been used for the disordered atoms that have been introduced in geometrically calculated positions and have been refined as rigid groups. The hydrogen atoms were not introduced.

The final reliability parameters are shown in Table 1, where R_1 , wR_2 , and S have the same meaning as in the preceding column and $w = 1/[\sigma^2(F_o^2) + (0.1454P)^2 + 15.38P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The reliability appears acceptable considering the poor quality of the crystal and the presence of disorder.

The crystals of $[\text{RuH}(\text{CO})_2(\text{py})_3][\text{BPh}_4]$ are colorless hexagonal prisms closed by hexagonal bipyramids. One of them was glued at the end of a glass fiber, and its diffraction pattern was studied on a Weissenberg camera using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The pattern showed well-shaped spots displaying hexagonal symmetry and a very long c period. The systematic extinctions suggested a primitive lattice with a 6_1 or 6_5 operator.

Accurate cell parameters and intensity data were collected on a Nonius CAD4 single-crystal diffractometer equipped with graphite-monochromatized Cu K α radiation. Crystal parameters and collection details are summarized in the fourth column of Table 1. Collection of three standard reflections every 97 measurements allowed one to exclude any crystal decay. The collected data were corrected for Lorentz and polarization effects and for absorption by using a ψ -scan method. The structure was solved by standard Patterson and Fourier methods in the $P6_5$ space group, and the absolute configuration of the crystal was chosen on the basis of Flack index.¹⁴ The hydrogen atoms were introduced in calculated positions and were allowed to ride on the connected carbon atoms. The final reliability indexes obtained in the last least-squares cycles, with all the heavy atoms with anisotropic thermal parameters, are shown in the last column of Table 1, where $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.09P]$ with $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

All calculations and drawings were performed by using the SHELXTL¹³ program.

Results and Discussion

Direct Detection of Intermediates during the CF₃COOH-Cocatalyzed WGSR. We recently evidenced that the nature of conjugated base affects the acid-cocatalyzed WGSR promoted by Rh₄(CO)₁₂.¹⁵ A role of the conjugated base is apparent also in the case, examined here, of the Ru₃(CO)₁₂ precursor in H₂O/diglyme solution: by comparison of two strong acids, *i.e.* sulfuric and triflic, as cocatalysts for the WGSR under the same conditions, only the former resulted in activity. Moreover, by the employment of CF₃COOH as cocatalyst in the 8 M H₂O/diglyme medium ($[\text{Ru}] = 0.036 \text{ M}$, $[\text{CF}_3\text{COOH}] = 0.5 \text{ M}$, $P_{\text{CO}} = 0.8 \text{ atm}$, $T = 95^\circ \text{C}$) the TOF(H₂) (TOF(H₂) = mol of H₂/mol of Ru/day) was 3 and increased to 18 on adding CF₃COOCs in a 1/5 molar ratio with respect to the acid. Such a sharp increase of TOF(H₂) demonstrates the beneficial role of CF₃COO[−] and can be understood by considering that CF₃COOH behaves as a weak acid in the reaction medium ($\kappa_a = 2 \times 10^{-2}$ at 25°C).¹⁶ Therefore, the addition of CF₃COOCs, although only in a 1/5 molar ratio with respect to the acid, strongly increases the concentration of its conjugated base.

Remarkably, the CF₃COO[−] concentration also affects the nature of the intermediate carbonyl complexes which accumulate during WGSR. At the low CF₃COO[−] concentration arising from the dissociation of CF₃COOH, only dimeric Ru(I) carbonyls, namely a P_{CO} -depending equilibrium mixture of Ru₂ $[\mu\text{-}\eta^2\text{-OC}(\text{CF}_3)\text{O}]_2(\text{CO})_6$ (**1a**) and Ru₂ $[\mu\text{-}\eta^2\text{-OC}(\text{CF}_3)\text{O}]_2(\text{CO})_4\text{L}_2$ ($\text{L} = \text{H}_2\text{O}$, diglyme) (**1b**),¹¹ can be detected by IR analysis after the early stages of catalysis (Figure 1a). When the CF₃COO[−] concentration is substantially increased by the addition of CF₃COOCs, however, two new absorptions (ν_{CO} 2136 and 2065

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(16) This value was determined by fitting the ¹⁹F NMR chemical shift data of progressively diluted CF₃COOH solutions (5×10^{-1} to $5 \times 10^{-4} \text{ M}$, 25°C) in diglyme containing 8 M H₂O, to equation which describes the dependence of the concentration C_0 on the measured chemical shift (Dimicoli, J. L.; Helene, C. J. *J. Chem. Soc.* **1973**, 95, 1036), affords the value of 2×10^{-2} .

(12) XSCANS: *X-ray Single Crystal Analysis System*, rel. 2.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

(13) Sheldrick, G. M. *SHELXTL-Plus*, Rel. 5.03; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

cm^{-1} ; Figure 1b) point out the accumulation of a new electrophilic carbonyl.

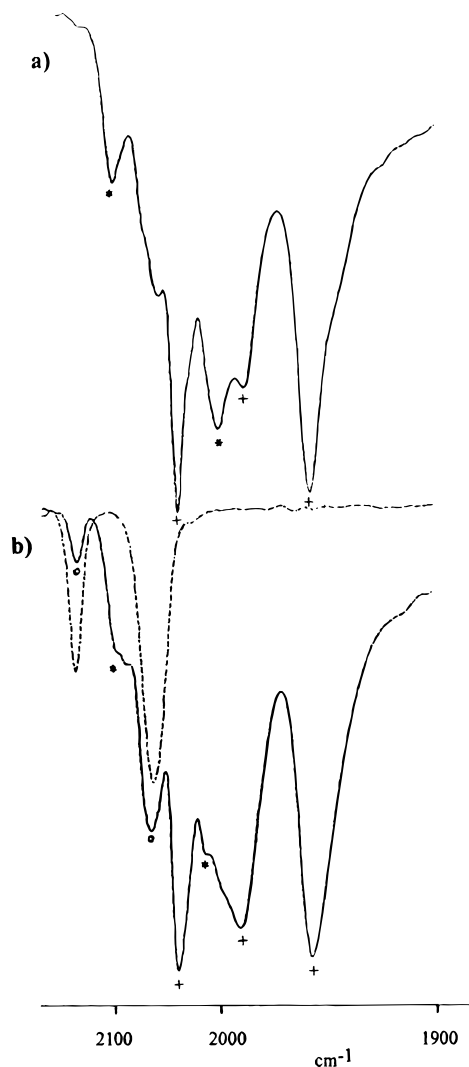


Figure 1. (a) IR spectrum in the CO stretching region of samples withdrawn during the WGS in diglyme containing 8 M H_2O ($[\text{Ru}] = 0.036 \text{ M}$, $[\text{CF}_3\text{COOH}] = 0.5 \text{ M}$, $P_{\text{CO}} = 0.8 \text{ atm}$, $T = 95^\circ\text{C}$). (b) IR spectrum in CO stretching region of samples withdrawn during the WGS at increased $[\text{CF}_3\text{COO}^-]$ by addition of CF_3COOH in a 1/5 molar ratio with respect to CF_3COOH . For a comparison, the spectrum of 0.015 M **2** in diglyme containing 8 M H_2O and 0.5 M CF_3COOH has been inserted (dashed line). The absorptions of the $\text{H}_2\text{O}/\text{CF}_3\text{COOH}$ /diglyme medium have been subtracted. Key: (*) absorptions of **1a**; (+) absorptions of (**1b**); (O) absorptions of **2**.

In order to characterize this latter species, WGS was carried out in a more concentrated solution at 95°C . On cooling of the sample to room temperature, a colorless precipitate, suitable for a single-crystal X-ray analysis, separated out. The IR spectra of this product in the solid state (ν_{CO} 2145 s, 2084 vs, and 2067 vs, cm^{-1}) and in an acidic H_2O /diglyme solution (Figure 1b, dashed line) confirm that it is the same carbonyl complex which is found to accumulate when the homogeneous catalysis is carried out in the presence of excess CF_3COO^- . The molecular structure shows that it is the cesium salt of $[\text{fac-Ru}(\text{OCOCF}_3)_3(\text{CO})_3]^-$ (**2**) (Figure 2); the main bond distances and angles are summarized in Table 2.

Reactions Interconverting the Intermediates and Producing CO_2 and H_2 . The formation of the equilibrium mixture of **1a,b**, the only products found to accumulate at low CF_3COO^- concentration (eq 1), parallels a number of well-known reactions

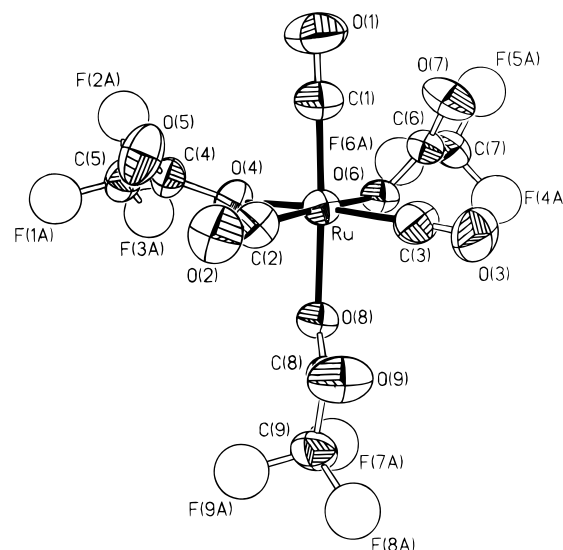
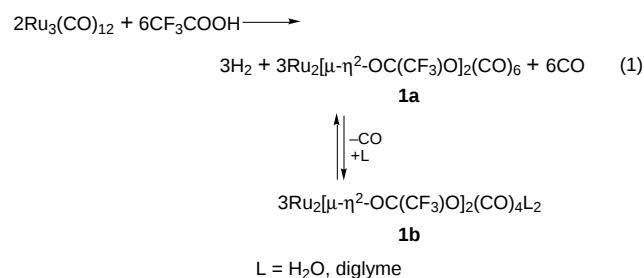


Figure 2. ORTEP projection of the structure of the anionic moiety of $[\text{fac-Ru}(\text{OCOCF}_3)_3(\text{CO})_3]\text{Cs}$ (**2**). Ru, C, and O atoms are represented by thermal ellipsoids at 50% probability. The disordered F atoms have been refined with isotropic thermal displacement factors and are here represented by spheres. For clarity, only one of the two limit positions of the fluorine atoms is shown.

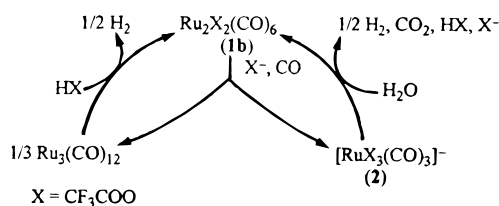
Table 2. Bond Lengths ($\text{\AA}$) and Angles (deg) for the Anion $[\text{fac-Ru}(\text{OCOCF}_3)_3(\text{CO})_3]^-$

Ru—C(1)	1.896(10)	O(4)—C(4)	1.267(10)
Ru—C(2)	1.914(10)	O(5)—C(4)	1.198(11)
Ru—C(3)	1.925(10)	C(4)—C(5)	1.520(11)
Ru—O(8)	2.088(6)	O(6)—C(6)	1.269(10)
Ru—O(4)	2.091(6)	O(7)—C(6)	1.213(11)
Ru—O(6)	2.096(6)	C(6)—C(7)	1.552(12)
C(1)—O(1)	1.142(11)	O(8)—C(8)	1.280(10)
C(2)—O(2)	1.130(11)	O(9)—C(8)	1.194(11)
C(3)—O(3)	1.107(11)	C(8)—C(9)	1.543(12)
C(1)—Ru—C(2)	89.5(4)	O(1)—C(1)—Ru	177.1(10)
C(1)—Ru—C(3)	92.8(4)	O(2)—C(2)—Ru	177.4(9)
C(2)—Ru—C(3)	90.2(4)	O(3)—C(3)—Ru	178.2(8)
C(1)—Ru—O(8)	174.1(3)	C(4)—O(4)—Ru	122.7(6)
C(2)—Ru—O(8)	93.2(3)	O(5)—C(4)—O(4)	129.1(9)
C(3)—Ru—O(8)	92.5(3)	O(5)—C(4)—C(5)	119.6(8)
C(1)—Ru—O(4)	92.8(4)	O(4)—C(4)—C(5)	111.2(7)
C(2)—Ru—O(4)	95.6(3)	C(6)—O(6)—Ru	123.1(6)
X(3)—Ru—O(4)	172.0(3)	O(7)—C(6)—O(6)	127.7(9)
O(8)—Ru—O(4)	81.7(2)	O(7)—C(6)—C(7)	119.5(8)
C(1)—Ru—O(6)	93.7(3)	O(6)—C(6)—C(7)	112.7(7)
C(2)—Ru—O(6)	175.5(3)	C(8)—O(8)—Ru	121.1(5)
C(3)—Ru—O(6)	92.8(4)	O(9)—C(8)—O(8)	129.0(9)
O(8)—Ru—O(6)	83.4(2)	O(9)—C(8)—C(9)	120.0(8)
O(4)—Ru—O(6)	81.1(2)	O(8)—C(8)—C(9)	111.0(7)

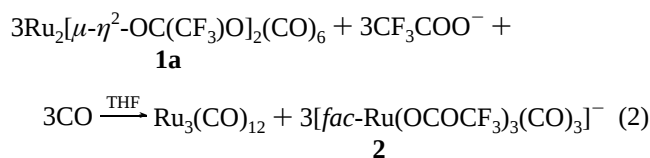
of $\text{Ru}_3(\text{CO})_{12}$ in the presence of carboxylic acids.²



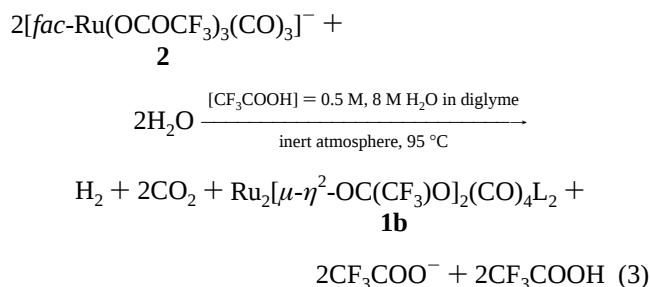
More surprising is the accumulation of the Ru(II) carbonyl **2** during the catalytic process with added CF_3COOCs . On the other hand, the high wavenumbers for the CO stretching vibrations of **2** indicate electrophilic character of the CO ligands as required for the WGS mandatory intermediate undergoing

Scheme 1. Overall Reactions Resulting in the Acid-Cocatalyzed WGSR Promoted by Ruthenium Carbonyls

attack by H₂O. An investigation on the origin of **2** and on its reaction with H₂O was then undertaken. As a result, we found that **2** is the product of a hitherto unrecognized disproportionation reaction of **1a**. In anhydrous THF, **1a** is stable under CO, while, under an inert atmosphere, **1b** is unaffected by excess CF₃COO[−]. When both these ligands are present, however, gas absorption takes place at room temperature; the disproportionation reaction is pointed out by the formation of orange insoluble Ru₃(CO)₁₂, while the characteristic IR absorptions of **2** become evident in the solution. Quantitative recovery of Ru₃(CO)₁₂ and **2** as well as gas volumetric measurement of reacted CO, indicate the stoichiometry of eq 2.



The reactions 1 and 2 account for the formation of the intermediates **1a,b** and **2**, which were found to accumulate during the catalytic process. Under catalytic conditions, Ru₃(CO)₁₂ becomes a labile intermediate. At low CF₃COO[−] concentrations, the disproportionation reaction 2 constitutes the slow step of the WGSR; on the other hand, CF₃COO[−] together with CO promotes the conversion of **1a** into the more labile **2**, till the enhanced process rate at high CF₃COO[−] concentrations is controlled by the reaction consuming **2**, *i.e.* by the reaction with H₂O which produces CO₂ and H₂. As a matter of fact, when **2** was warmed under an inert atmosphere to the same temperature (95 °C) and in the same medium of the catalytic process, H₂ and CO₂ were produced in a 1/2 ratio, together with **1b** which was identified on the basis of its IR spectrum (eq 3).



Reactions 1–3 result altogether in a catalytic cycle (Scheme 1) producing CO₂ and H₂ from CO and H₂O.

Origins and Nature of the Hydrido Intermediates for Dihydrogen Formation. The distinctive aspect of such a WGSR (Scheme 1) is that Ru(0) and a CO ligand in a Ru(II) complex alternate in supplying electrons for dihydrogen formation. Since the knowledge of the ruthenium hydrides which arise from Ru₃(CO)₁₂ in acidic media can be of general utility for a better understanding of several catalytic reactions besides WGSR, we devoted a particular effort to identify the hydrido

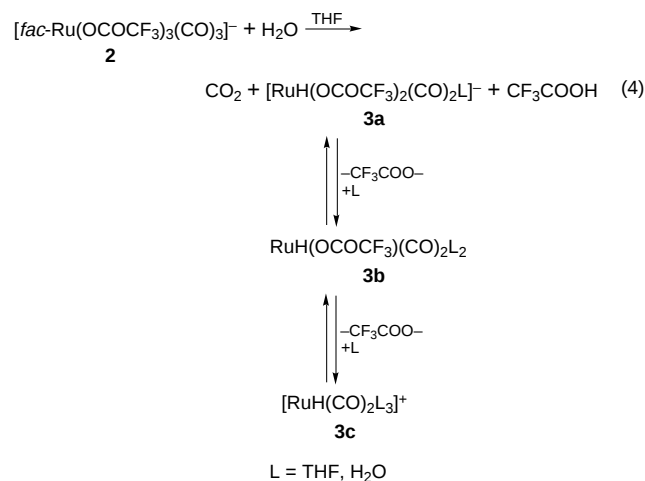
intermediates in the two reductions of the proton respectively in the left- and right-hand branches of Scheme 1.

(a) From Ru₃(CO)₁₂ and HX. In the case of H₂ being formed from Ru₃(CO)₁₂ and CF₃COOH, it has been shown that the mononuclear hydrido Ru(II) complex [RuH(OCOCF₃)(CO)₂(py)₂] can be trapped when the N-donor ligand pyridine is present.¹⁷ By analogy, we assume that the more labile RuH(OCOCF₃)(CO)₂L₂ (L = H₂O or diglyme) (**3b**) is formed *via* oxidative addition of CF₃COOH to Ru₃(CO)₁₂ under the conditions of catalysis and constitutes the intermediate for the dihydrogen production of the left-hand branch of Scheme 1. More details on dihydrogen evolution from **3b** are given in section b, since the low-temperature reaction between **2** and H₂O in neutral solution allows this intermediate to be synthesized and, thus, its properties to be separately investigated.

(b) From **2 and H₂O.** As mentioned before, reaction 3 between **2** and 8 M H₂O in diglyme requires high temperatures to occur when tested in the same medium of catalysis, *i.e.* in the presence of 0.5 M CF₃COOH. However, in the absence of acid, **2** undergoes nucleophilic attack by H₂O already at room temperature, and hydrido intermediates can be detected under these milder conditions. The addition of water to 0.036 M **2** in diglyme at 20 °C brings about modifications in the IR spectrum of the solution: the absorptions of **2** are replaced by two bands at 2041 and 1957 cm^{−1}, indicative for a *cis*-dicarbonyl complex, and one at 2338 cm^{−1}, this latter being due to the produced CO₂. The reaction is complete in 45 min; no dihydrogen is formed under these conditions, thus suggesting that the production of CO₂ leaves a stable hydrido *cis*-dicarbonyl complex of Ru(II). Any attempt to isolate this species failed, and its nature was ascertained by chemical and spectroscopic methods.

When the reaction between **2** and H₂O was carried out in THF-*d*₈ ([**2**] = 0.4 M, [H₂O] = 8 M), the ¹H NMR spectrum of the resulting solution showed a hydridic peak at −13.8 ppm, accompanied by two minor resonances at −13.4 and −14.0 ppm (Figure 4a).

By analogy with the recently reported case of the hydridosulfonatocarbonyl(pyridine)ruthenium(II),¹⁷ the three resonances were tentatively attributed to an equilibrium mixture of anionic, neutral, and cationic Ru(II) hydrido dicarbonyl complexes formed by different degrees of substitution of trifluoroacetato by neutral H₂O or THF ligands (eq 4).



In order to confirm that, we examined how the CF₃COO[−] relative concentration affects the three resonances. The case of [CF₃COO[−]]/[Ru] = 2 was investigated by reacting with H₂O

(17) Fachinetti, G.; Funaioli, T.; Marchetti, F. *J. Organomet. Chem.* **1995**, 498, C20.

in ethers $\{fac\text{-Ru}(\text{OCOCF}_3)_2(\text{CO})_3[(\text{CH}_3)_2\text{CHOH}]\}$ (**4**), whose molecular structure is reported in Figure 3.

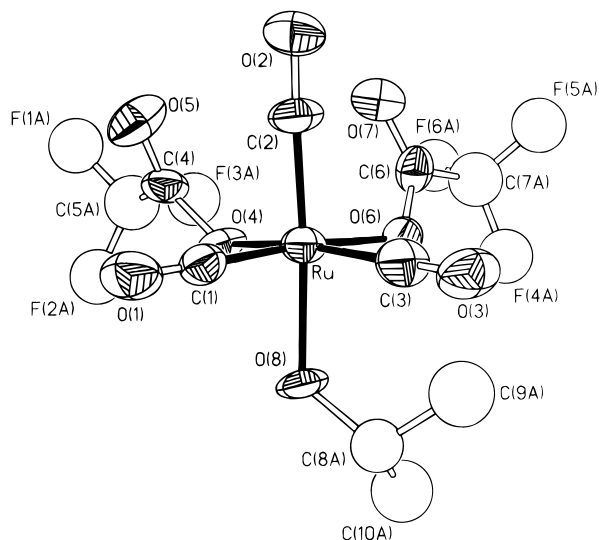


Figure 3. 3. ORTEP projection of the molecular structure of $\{fac\text{-Ru}(\text{OCOCF}_3)_2(\text{CO})_3[(\text{CH}_3)_2\text{CHOH}]\}$ (**4**). Thermal ellipsoids are represented at 30% probability. The disordered CF_3 and $\text{C}(\text{CH}_3)_2$ groups have been refined with isotropic thermal parameters and are represented by spheres. Moreover, to limit superposition, only one of the two limit positions is shown. The distances and angles around the metal are as follows: Ru—C(2) 1.85(3), Ru—C(1) 1.86(3), Ru—C(3) 1.91(3), Ru—O(4) 2.02(2), Ru—O(6) 2.06(2), Ru—O(8) 2.092(13), C(2)—Ru—C(1) 88.0(12), C(2)—Ru—C(3) 90.9(11), C(1)—Ru—C(3) 91.6(12), C(2)—Ru—O(4) 96.9(9), C(1)—Ru—O(4) 94.4(9), C(3)—Ru—O(4) 170.3(9), C(2)—Ru—O(6) 97.1(10), C(1)—Ru—O(6) 174.7(8), C(3)—Ru—O(6) 89.8(10), O(4)—Ru—O(6) 83.6(6), C(2)—Ru—O(8) 175.6(9), C(1)—Ru—O(8) 90.9(9), C(3)—Ru—O(8) 93.4(9), O(4)—Ru—O(8) 79.0(6), O(6)—Ru—O(8) 83.9(6).

The neutral electrophilic carbonyl complex **4** (ν_{CO} (Nujol): 2153 s, 2094 vs, and 2078 vs cm^{-1}) reacted at room temperature with 8 M H_2O in diglyme at a rate comparable to **2**; the IR spectrum of the solution at the end of the reaction (ν_{CO} : 2041 and 1957 cm^{-1}) shows only minor modifications with respect to that arising from the reaction between **2** and H_2O .

When the reaction between **4** and H_2O is carried out in THF-d_8 , however, the ^1H NMR spectrum of the resulting solution shows only the two hydridic resonances at -13.4 and -13.8 ppm (Figure 4b), while the third resonance at -14.0 ppm becomes evident only when CF_3COOCs is added to the solution: the three NMR resonances, in a ratio identical to that in Figure 4a from the reaction between **2** and H_2O , are observed when CF_3COOCs is added in equimolar amount with respect to Ru. In a separate experiment we examined the effect of the added strong acid $\text{CF}_3\text{SO}_3\text{H}$ onto the spectrum of Figure 4b. Under the hypothesis that the equilibria in (**4**) are responsible for the three hydridic resonances, it is expected that the addition of an acid (strong enough to protonate the trifluoroacetate ions released in the solution) results in the accumulation of the cationic species. Accordingly, the addition of increasing amounts of triflic acid enhances the most downfield resonance, as shown in Figure 4c–f. Being that the molar ratio $\text{CF}_3\text{SO}_3\text{H}/\text{Ru} = 2.40$, the two IR bands at 2041 and 1957 cm^{-1} observed at the end of the reaction between **4** (or **2**) and H_2O are shifted to higher frequencies (2047 and 1963 cm^{-1}), as a consequence of the $\text{CF}_3\text{SO}_3\text{H}$ -promoted accumulation of the cationic species. These findings demonstrate the intervention of CF_3COO^- ligands in generating the three hydrido species from **2** and H_2O , and it is likely that the three resonances at -14.0 , -13.8 , and -13.4 ppm (Figure 4a) are attributable to **3a**, **3b**, and **3c**,

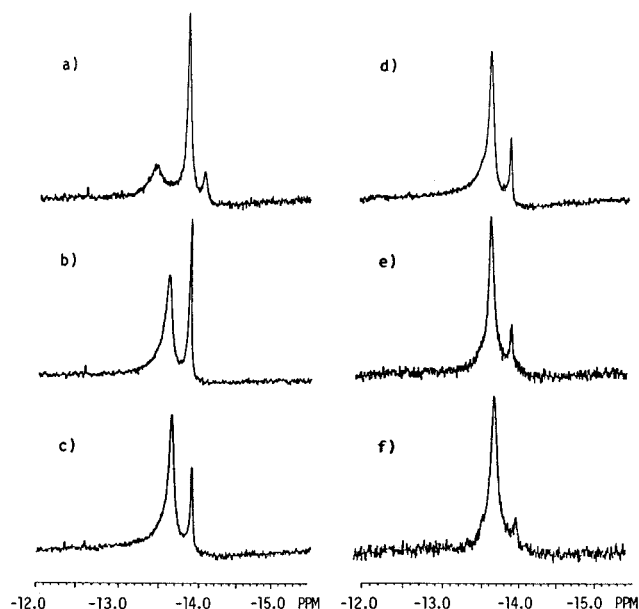


Figure 4. ^1H NMR spectra of hydrides accumulating at room temperature in the reaction between Ru(II) carbonyls and H_2O in THF-d_8 : (a) Same spectrum obtained directly from **2** or on adding CF_3COOCs to the hydride mixture arising from **4**; (b) spectrum obtained directly from **4**; (c–f) spectra showing the modifications induced on adding increasing amounts of triflic acid to the solution of spectrum b.

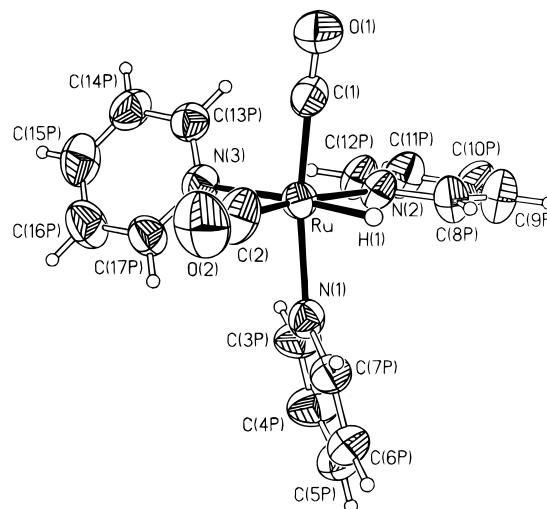


Figure 5. Projection of the cation in the structure of $[\text{RuH}(\text{CO})_2(\text{py})_3]^+[\text{BPh}_4]^-$. Thermal ellipsoids are represented at 50% probability.

respectively. All the three are *cis*-dicarbonyl hydrido complexes; moreover, hydride chemical shifts of less than -10 ppm exclude the presence of CO groups trans to the hydrido ligand.¹⁸ Remarkably, while the neutral **3b** is the dominant species in a neutral solution, the addition of a strong acid to the mixture of hydrido complexes converts **3a** and **3b** into **3c**, a conclusion which will be reviewed again in the next section.

Finally, the nature of the hydrido complexes arising from the nucleophilic attack of H_2O onto **2** or **4** has been proven by treating their mixture with pyridine, which nearly quantitatively converts **3a–c** into the isolable and structurally characterized hydrido cationic complex $[fac\text{-RuH}(\text{CO})_2(\text{py})_3]^+$,¹⁷ whose structure is shown in Figure 5 with the main bond distances and angles in Table 3.

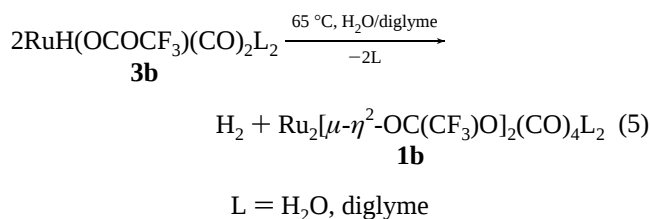
Dihydrogen Formation from 3a–c. As required in the overall reaction 3, dihydrogen production from the mixture of

Table 3. Bond Lengths (Å) and Angles (deg) for the Cation [RuH(CO)₂(py)₃]⁺

Ru—C(1)	1.850(7)	C(6P)—C(7P)	1.362(9)
Ru—C(2)	1.861(7)	N(2)—C(12P)	1.334(7)
Ru—N(1)	2.149(5)	N(2)—C(8P)	1.339(7)
Ru—N(2)	2.185(5)	C(8P)—C(9P)	1.379(9)
Ru—N(3)	2.284(4)	C(9P)—C(10P)	1.351(9)
Ru—H(1)	1.58 ^a	C(10P)—C(11P)	1.379(9)
C(1)—O(1)	1.141(8)	C(11P)—C(12P)	1.369(8)
C(2)—O(2)	1.145(7)	N(3)—C(13P)	1.330(8)
N(1)—C(3P)	1.343(7)	N(3)—C(17P)	1.344(8)
N(1)—C(7P)	1.350(7)	C(13P)—C(14P)	1.387(7)
C(3P)—C(4P)	1.361(9)	C(14P)—C(15P)	1.347(11)
C(4P)—C(5P)	1.361(9)	C(15P)—C(16P)	1.376(11)
C(5P)—C(6P)	1.363(9)	C(16P)—C(17P)	1.380(8)
C(1)—Ru—C(2)	87.2(3)	C(7P)—C(6P)—C(5P)	119.3(6)
C(1)—Ru—N(1)	170.2(2)	N(1)—C(7P)—C(6P)	123.6(6)
C(2)—Ru—N(1)	94.2(3)	C(12P)—N(2)—C(8P)	117.1(5)
C(1)—Ru—N(2)	93.7(2)	C(12P)—N(2)—Ru	124.5(4)
C(2)—Ru—N(2)	171.0(2)	C(8P)—N(2)—Ru	118.5(4)
N(1)—Ru—N(2)	83.4(2)	N(2)—C(8P)—C(9P)	121.9(6)
C(1)—Ru—N(3)	97.5(2)	C(10P)—C(9P)—C(8P)	120.5(6)
C(2)—Ru—N(3)	95.5(2)	C(9P)—C(10P)—C(11P)	118.1(6)
N(1)—Ru—N(3)	92.0(2)	C(12P)—C(11P)—C(10P)	118.8(6)
N(2)—Ru—N(3)	93.3(2)	N(2)—C(12P)—C(11P)	123.6(6)
O(1)—C(1)—Ru	174.5(5)	C(13P)—N(3)—C(17P)	117.3(5)
O(2)—C(2)—Ru	175.2(6)	C(13P)—N(3)—Ru	121.4(4)
C(3P)—N(1)—C(7P)	115.4(5)	C(17P)—N(3)—Ru	120.6(4)
C(3P)—N(1)—Ru	123.0(4)	N(3)—C(13P)—C(14P)	122.8(7)
C(7P)—N(1)—Ru	121.2(4)	C(15P)—C(14P)—C(13P)	119.0(7)
N(1)—C(3P)—C(4P)	123.6(6)	C(14P)—C(15P)—C(16P)	119.8(6)
C(5P)—C(4P)—C(3P)	119.6(6)	C(15P)—C(16P)—C(17P)	118.2(8)
C(4P)—C(5P)—C(6P)	118.4(6)	N(3)—C(17P)—C(16P)	122.9(6)

^a The H(1) atom coordinates have been refined with constraints.

hydrides **3a–c** is expected, and we investigated the required conditions for that. Under an inert atmosphere, 0.05 M **4** was reacted at room temperature with 8 M H₂O in diglyme, till CO₂ production ceased. By the increase of the temperature to 65 °C, dihydrogen evolved from the solution, and the reaction was monitored by determining the H₂/Ru molar ratio at various stages. It can be seen from Figure 6 that its limit value is 0.5, thus indicating the reductive elimination (eq 5), which involves only hydrido ligands and no active hydrogen atoms from the medium.



According to reaction 5, IR absorptions at 2043, 1989, and 1958 cm⁻¹ after a long reaction time revealed that **1b** is the product accompanying dihydrogen formation. The intervention of active hydrogen atoms from the medium was excluded even in acidic solution. As mentioned before, rather than giving rise to H₂, CF₃SO₃H converts hydrides **3a,b** into the cationic species **3c**, which was found inert toward H₂ formation. As a matter of fact, we observed that at 65 °C dihydrogen production slows down on increasing the amount of added acid (Figure 6). It stops for [CF₃SO₃H]/[Ru] = 5; a temperature of 95 °C was then required for restoring slow H₂ production.

On these grounds we exclude that dihydrogen formation in the overall reaction 3 is the result of simple protonation of the hydrido intermediate complexes. More probably, the dihydrogen-eliminating intermediate has the nature of a trifluoroacetato-

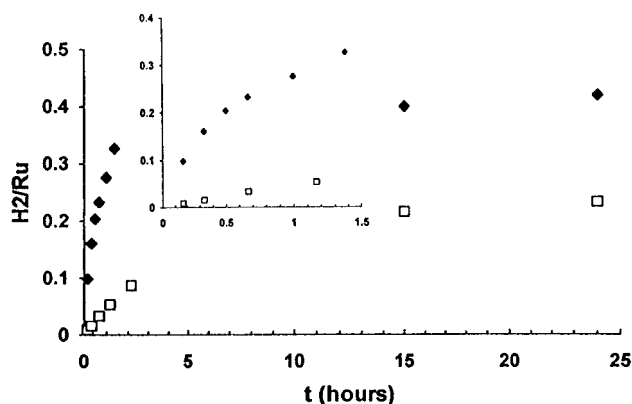
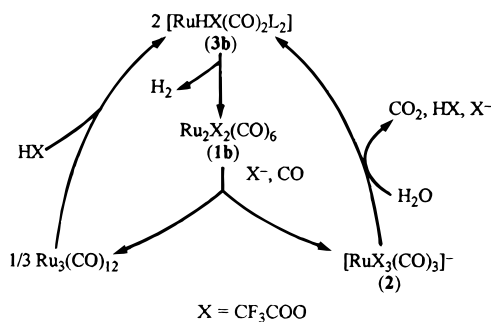


Figure 6. Dihydrogen evolution at 65 °C from the mixture of hydrides **3a–c** ([Ru] = 0.05 M). Plots of the H₂/Ru molar ratio vs time, with (□) and without (♦) added 0.075 M CF₃SO₃H.

Scheme 2. Fundamental Chemistry of Ruthenium Carbonyls in Acidic Media



bridged diruthenium dihydrido complex, whose sulfinate-bridged analog has been fully characterized.¹⁹

Conclusions. By including the findings on the origin and stability of the hydrido intermediates into the cycle drawn in Scheme 1, we can summarize the chemistry of ruthenium carbonyls in acidic media²⁰ as in Scheme 2.

The same hydrido intermediate **3b** is formed in two distinct reactions, namely the oxidative addition of the acid to Ru₃(CO)₁₂ and the nucleophilic attack by H₂O onto a CO ligand in **2**, followed by CO₂ elimination from the metal hydroxycarbonyl. The role attributed to an acidic cocatalyst for WGS is generally the protonation of a hydrido intermediate to produce dihydrogen.²¹ On the contrary, in the present case H⁺ hampers dihydrogen evolution from the mixture of hydrides **3a–c** as well as nucleophilic attack by water onto **2**: the only role here recognized for acidity is in the oxidative addition of HX to Ru₃(CO)₁₂. On the other hand, the hitherto neglected intervention of the conjugated base is critical in promoting the disproportionation reaction of **1a**, and is required for the formation of the higher oxidation state complex **2**, whose CO ligands can undergo nucleophilic attack by water. The need for a coordinating conjugated base which assists the disproportionation reaction renders the exceptionally strong acid CF₃SO₃H

(19) Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 1345.

(20) The conclusions of the present work are likely to apply also in the case of H₂SO₄, the first employed acidic cocatalyst for the WGS. In fact, IR absorptions due to dinuclear Ru(I) carbonyl complexes analogous to **1a** or **1b** (ν_{CO} : 2063 m, 2042 s, 2004 m, and 1959 s cm⁻¹) and to a Ru(II) carbonyl complex analogous to **2** (ν_{CO} : 2154 m and 2083 s cm⁻¹) were detected during a catalytic run carried out in diglyme under the following conditions: [Ru] = 0.036 M, [H₂O] = 8 M, [H₂SO₄] = 0.8 M, T = 95 °C, P_{CO} = 0.9 atm.

(21) (a) Ford, P. C.; Ungermann, C.; Landis, V.; Moya, S. A.; Rinker, R. C.; Laine, R. M. *Adv. Chem. Ser.* **1979**, No. 173, 81. (b) Laine, R. C.; Crawford, E. J. *J. Mol. Catal.* **1988**, *44*, 357.

unsuitable as a cocatalyst for WGS, contrary to H_2SO_4 , because of the coordinating power of SO_4^{2-} . A similar role for the disproportionation reaction was ascertained also in the acid-cocatalyzed WGS promoted by rhodium carbonyls in pyridine.¹⁵

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dissociation constant, Dr. U. Englert, Aachen University, Aachen, Germany, for intensity data collection on a $[\text{RuH}(\text{CO})_2(\text{py})_3][\text{BPh}_4]$ single crystal, Mr. F. Del Cima for technical assistance, and Chimet SpA for a gift of ruthenium.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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