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Ruthenium, Rhodium, and Iridium α -Diimine Complexes as Precatalysts in Carbon Dioxide Hydrogenation and Formic Acid Decomposition

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Abstract

This study describes a series of water-soluble half-sandwich ruthenium(II), rhodium(III), and iridium(III) complexes with α -diimine ligands containing substituted aromatic groups. These ligands were derived from glyoxal and 2-aminophenol (**a**), 4-methyl-2-aminophenol (**b**), 4-aminophenol (**c**), phenyl hydrazine (**d**), and 1-aminonaphthalene (**e**). The ruthenium(II) (**1b–1e**), rhodium(III) (**2a–2c**, **2e**), and iridium(III) complexes (**3a–3e**) were obtained by reacting the ligands (**a–e**) with the corresponding dimeric precursor $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ ($p\text{-cym}$ = p -cymene) or $[(\eta^5\text{-Cp}^*)\text{MCl}_2]_2$ (Cp^* = pentamethylcyclopentadienyl, M = Rh, Ir) in air and under nonanhydro conditions. The air-stable and water-soluble ruthenium(II), rhodium(III), and iridium(III) complexes were characterized via nuclear magnetic resonance spectroscopy and electrospray ionization–mass spectrometry. The structures of complexes $[(\eta^6\text{-}p\text{-cym})\text{Ru}(\text{d})\text{Cl}]\text{Cl}$, **1d**; $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{a})\text{Cl}]\text{Cl}$, **3a**; and $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{c})\text{Cl}]\text{Cl}$, **3c** were determined via single-crystal X-ray diffraction. Additionally, the complexes exhibited catalytic activity as precatalysts in formic acid decomposition. Complex $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{d})\text{Cl}]\text{Cl}$, **3d** achieved turnover number (TON) and turnover frequency (TOF) values of up to 2150 and 3861 h^{-1} , respectively, at short reaction times. In the hydrogenation of carbon dioxide, $[(\eta^6\text{-}p\text{-cym})\text{Ru}(\text{e})\text{Cl}]\text{Cl}$, **1e** attained TON and TOF values of up to 1385 and 69.25 h^{-1} , respectively.

Keywords: carbon dioxide hydrogenation; formic acid decomposition; catalysis; transition metal complexes; α -diimine ligands



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1. Introduction

The activation of small, low-reactivity molecules such as carbon dioxide is an area of growing interest owing to its economic and environmental implications. Specifically, the use of CO_2 as a C1 feedstock for producing fuels and chemicals is becoming an increasingly attractive strategy to reduce the carbon footprint in the chemical and energy sectors [1]. Meanwhile, formic acid (FA) has been proposed as an energy carrier and a potential chemical hydrogen storage system [2,3].

Accordingly, intensive efforts have been directed toward developing efficient catalysts to produce FA via CO₂ hydrogenation and FA decomposition to generate H₂. Several reviews in these two areas have effectively summarized recent work [4], for example, about FA dehydrogenation with homogeneous and heterogeneous systems, including high-pressure H₂ generation [5], and carbon dioxide hydrogenation by different types of catalysts addressing reactive capture of CO₂ [5,6].

Inoue et al. first reported the homogeneous catalytic hydrogenation of CO₂ to FA [7]. Since then, numerous complexes of ruthenium, rhodium, and iridium have been investigated. For several decades, systems were designed such that all transformations occurred at the metal center, with ligands acting only as spectators [8]. However, in recent years, catalytic systems have been developed with the active participation of auxiliary ligands, enabling the creation of highly active catalytic systems for CO₂ reduction.

Recent studies have shown that ruthenium(II) and iridium(III) complexes containing proximal protic groups can catalyze the hydrogenation of CO₂ to produce formate and promote FA decomposition to H₂ and CO₂ [9]. It has been proposed that these ligands with protic functional groups near the metal can accelerate proton-transfer events in various reactions.

For example, an iridium(III) complex with a (2,2'-dihydroxy)bipyridine ligand is active in CO₂ hydrogenation at 115 °C for 18 h, with turnover number (TON) = 2270 and turnover frequency (TOF) = 126 h⁻¹. The ruthenium(II) analog to the previous complex, featuring a *p*-cymene auxiliary ligand, is active under the same conditions, with TON = 1070 and TOF = 59.4 h⁻¹ [9], while an iridium(III) complex with the mixed NHC-hydroxypyridine ligand is almost as active as the first example, yielding a TON = 2020 and TOF = 112 h⁻¹ [9]. A unique feature of the last two systems is that the same catalysts are active in the decomposition of FA at 60 °C for 3 h, showing modest values for the ruthenium (2,2'-dihydroxy)bipyridine complex (TON = 45, TOF = 15 h⁻¹) and iridium NHC-hydroxypyridine complex (TON = 180, TOF = 59 h⁻¹) and even higher values for the iridium(III) (2,2'-dihydroxy)bipyridine complex (TON = 3500, TOF = 1200 h⁻¹).

Some of the most efficient homogeneous systems for CO₂ hydrogenation include ruthenium complexes [(PNP³)Ru(H)Cl(CO)] (TON = 200,000; TOF = 1,100,000 h⁻¹) [10] and [(η⁶-*p*-cym)Ru(bis-NHC¹)Cl]PF₆ (TON = 23,000; TOF = 300 h⁻¹) [11] and iridium complexes [(PNP¹)IrH₃] (TON = 3,500,000; TOF = 73,000 h⁻¹) [12] and [Ir(bis-NHC²)(AcO)I₂] (TON = 190,000; TOF = 2500 h⁻¹) [13]. On the other hand, for the FA dehydrogenation reaction, some systems show high efficiency in H₂ production, such as ruthenium complexes [RuCl₂(C₆H₆)]₂/DPPE (TON > 1,000,000; TOF = 1000 h⁻¹) [14] and [(PNP³)Ru(H)Cl(CO)] (TON = 706,500; TOF = 256,000 h⁻¹) [10] and iridium complexes [Cp*Ir(pyrimidyl imidazoline)H₂O]SO₄ (TON = 68,000; TOF = 322,000 h⁻¹) [15] and [Cp*Ir(PHEN-diol)H₂O]SO₄ (TON = 5,000,000; TOF = 1900 h⁻¹) [16].

Other systems studied in these catalytic reactions involve recent applications such as the Ru-PNP/liquid ionic system, which is used in CO₂ hydrogenation-dehydrogenation catalysis [17], a low-coordinate Cp*Ir complex with a donor-flexible O,N-ligand for FA dehydrogenation [18], and a Mn-pincer complex in the presence of lysine, used in the reversible hydrogenation of CO₂ to FA [19], as well as several heterogeneous systems that were used in the production of H₂ from the decomposition of FA, for example, a CuO-CeO₂/γ-Al₂O₃ catalyst [20], a photocatalyst of copper oxide [21], and gold nanoparticles supported on a porous polymer matrix [22]. In the hydrogenation of CO₂ to FA, a system of iridium immobilized in solid phosphines has been used under base-free conditions [23]. However, in these heterogeneous catalyst systems, substrate conversion efficiencies are still low.

Separately, α -diimine complexes of late transition metals have been extensively studied as catalysts in ethylene homopolymerization and copolymerization [24]. Although many studies have explored α -diimine metal complexes, relatively few have focused on their use in CO₂ catalytic hydrogenation and FA decomposition. In one study, complexes of ruthenium(II), rhodium(III), and iridium(III) with an α -diimine ligand derived from *p*-aminobenzoic acid acted as precatalysts in the hydrogenation of CO₂ to produce formate, with the best conversion achieved being a TOF of 35 h^{−1} within 2 h and a TON of 322 for the ruthenium complex, using DBU as a base at 120 °C and 60 bar [25]. In another study, a ruthenium(II) complex with an α -diimine ligand derived from *p*-aminophenol was synthesized and evaluated for cytotoxic activity [26].

These findings prompted us to investigate half-sandwich ruthenium(II), rhodium(III), and iridium(III) complexes with α -diimine ligands containing protic groups as precatalysts for the direct hydrogenation of CO₂ to yield formate and the decomposition of FA to H₂ and CO₂ in aqueous solution. Both reactions were performed without excluding air or moisture, enhancing their relevance to sustainable energy and chemical feedstock development.

2. Experimental Section

All manipulations were performed in air using undried solvents that were only distilled before use through standard procedures. All the chemicals were used as received from Merck Sigma-Aldrich. The dimeric precursors [(η^6 -*p*-cym)RuCl₂]₂, [(η^5 -Cp*)MCl₂]₂ (M = Rh, Ir) were synthesized according to reported methods [27,28]. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 298 K using a JEOL-ECA 600 MHz spectrometer with the “single-pulse” technique, as well as a Bruker Ascend 750 MHz instrument. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. Electrospray ionization–mass spectrometry (ESI-MS) histograms were obtained using a 6410B Agilent Technologies triplet quadrupole mass spectrometer, with electrospray as the ionization method. IR spectra were measured using a Thermo Scientific Nicolet iS5 equipped with iD5 ATR accessory. Thermograms were recorded in a Discovery DSC, TA Instruments system. Single crystals of C₂₄H₂₈Cl₂N₄Ru (**1d**) and C₂₄H₂₇N₂O₂Cl₂Ir (**3c**) were obtained from acetone/water, while single crystals of C₂₄H₂₉Cl₂IrN₂O₃ (**3a**) were obtained from water. Suitable crystals of the complexes were selected and diffracted on an Xcalibur Atlas Gemini diffractometer. The crystals were kept at 293 K during data collection. The structure was solved using Olex2 [29] with the SHELXT [30] structure solution program via intrinsic phasing, and refined with the SHELXL [31] refinement package through least squares minimization.

The hydrogenation of CO₂ was carried out in a stainless-steel high-pressure reactor (Parr®, Parr Instrument Company, Moline, IL, USA). The decomposition of FA in aqueous media was performed in a Monowave 50 synthesis reactor (Anton Paar®, Anton Paar GmbH, Graz, Austria).

2.1. General Procedure for the Synthesis of the α -Diimine Ligands **a–e**

The aromatic primary amine (2 equivalents) was dissolved in methanol (30 mL) using a 50 mL round-bottom flask. Subsequently, aqueous glyoxal (40%, 1.1 equivalents) was added. The reaction mixture was heated at 65 °C for 1.5 h under an open atmosphere. The mixture was then cooled to room temperature, and the formed solid was filtered off and then washed with cold methanol (3 × 5 mL) and diethyl ether (3 × 5 mL). Finally, the solid was dried under reduced pressure. The ligands **a**, **c**, and **d** have previously been reported in the literature [26,32,33].

Cyclic tautomer of N,N'-bis(2-hydroxyphenyl)ethane-1,2-diimine, **a**

Compound **a** (Chart 1) was obtained as a white solid from 2-aminophenol (2.0 g, 18.3 mmol) and aqueous glyoxal (40%, 1.16 mL, 10 mmol). Yield: 92% (2.03 g, 8.44 mmol). M. p. 210–211 °C. The chemical shifts conform to the data reported in the literature [32]. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz): 7.32 (d, 2H, $^3J_{\text{H-H}} = 4.58$, NH), 6.77 (t, 2H, $^3J_{\text{H-H}} = 7.78$, CH_{ar}), 6.73 (d, 2H, $^3J_{\text{H-H}} = 6.72$, CH_{ar}), 6.68 (d, 2H, $^3J_{\text{H-H}} = 6.68$, CH_{ar}), 6.63 (t, 2H, $^3J_{\text{H-H}} = 6.62$, CH_{ar}), 5.29 (d, 2H, $^3J_{\text{H-H}} = 4.12$, CHSp^3). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ ppm): 143.98 (O- C_{ar}), 132.83 (N- C_{ar}), 124.07 (CH_{ar}), 121.35 (CH_{ar}), 118.76 (CH_{ar}), 116.89 (CH_{ar}), 77.98 (CHSp^3). $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$, Calc. 240.09. ESI-MS, (m/z): 240.9 [M^+]. FT-IR(ATR): 3372 (N-H), 1610 cm^{-1} (C-N).

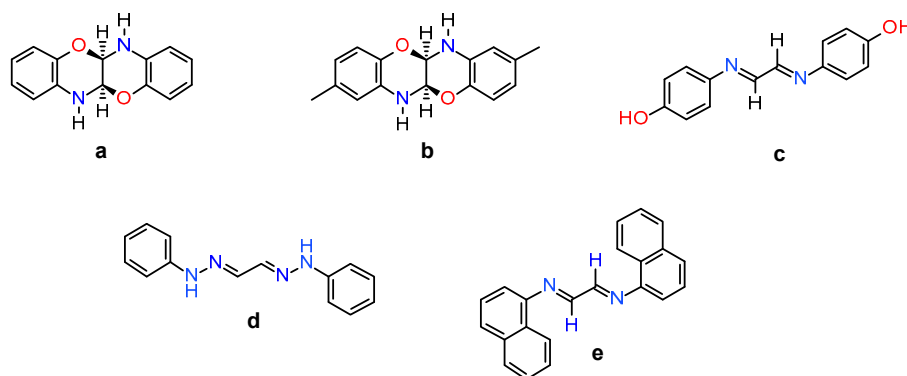


Chart 1. Structures of ligands **a–e**.

Cyclic tautomer of $\text{N,N}'$ -bis[(2-hydroxy-5-methyl)phenyl]ethane-1,2-diimine, **b**

Compound **b** (Chart 1) was obtained as a white solid from 4-methyl-2-aminophenol (2.0 g, 16.23 mmol) and aqueous glyoxal (40%, 1.02 mL, 8.9 mmol). Yield: 95.7% (2.08 g, 7.76 mmol). M. p. 225–226 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ ppm): 7.18 (d, 2H, $^3J_{\text{H-H}} = 4.12$, NH), 6.53 (d, 2H, $^3J_{\text{H-H}} = 7.78$, CH_{ar}), 6.50 (d, 2H, $^4J_{\text{H-H}} = 1.37$, CH_{ar}), 6.40 (dd, 2H, $^3J_{\text{H-H}} = 8.24$, $^4J_{\text{H-H}} = 1.37$, CH_{ar}), 5.19 (d, 2H, $^3J_{\text{H-H}} = 4.12$, CHSp^3), 2.16 (s, 6H, CH_3). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ ppm): 139.6 (O- C_{ar}), 130.53 (N- C_{ar}), 130.33 (CH_3 - C_{ar}), 119.47 (CH_{ar}), 116.22 (CH_{ar}), 115.05 (CH_{ar}), 75.81 (CHSp^3), 20.97 (CH_3). $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$, Calc. 268.12. ESI-MS, (m/z): 269.1 [M^+]. FT-IR(ATR): 3494 (N-H), 1623 cm^{-1} (C-N).

$\text{N,N}'$ -bis(4-hydroxyphenyl)ethane-1,2-diimine, **c**

Compound **c** (Chart 1) was obtained as an orange solid from 4-aminophenol (2.0 g, 18.3 mmol) and aqueous glyoxal (40%, 1.16 mL, 10 mmol). Yield: 98.0% (2.07 g, 8.96 mmol). M. p. 231–232 °C. The chemical shifts conform to the data reported in the literature [26]. ^1H NMR (DMSO- d_6 , 750 MHz, δ ppm): 9.78 (s, 2H, OH), 8.41 (s, 2H, N-CH), 7.32 (d, 4H, $^3J_{\text{H-H}} = 8.70$, CH_{ar}), 6.82 (d, 4H, $^3J_{\text{H-H}} = 9.16$, CH_{ar}). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ ppm): 160.49 (N=CH), 159.13 (O- C_{ar}), 143.89 (N- C_{ar}), 126.05 (CH_{ar}), 118.59 (CH_{ar}). $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$, Calc. 240.09. ESI-MS, (m/z): 241.1 [M^+]. FT-IR(ATR): 3016 (O-H), 1600 cm^{-1} (C=N).

$\text{N,N}'$ -bis(phenylhydrazine)ethane-1,2-diimine, **d**

Compound **d** (Chart 1) was obtained as a yellow solid from phenylhydrazine (2.0 g, 13.8 mmol) and aqueous glyoxal (0.9 mL, 7.6 mmol). Yield: 92.3% (1.52 g, 6.38 mmol). M. p. 147–148 °C. The chemical shifts conform to the data reported in the literature [33]. ^1H NMR (DMSO- d_6 , 750 MHz, δ ppm): 10.42 (s, 2H, NH), 7.76 (s, 2H, N-CH), 7.24 (t, 4H, $^3J_{\text{H-H}} = 7.32$, CH_{ar}), 7.07 (d, 4H, $^3J_{\text{H-H}} = 8.70$, CH_{ar}), 6.79 (t, 2H, $^3J_{\text{H-H}} = 7.32$, CH_{ar}). ^{13}C -RMN (DMSO- d_6 , 189 MHz, δ ppm): 145.32 (N=CH), 137.44 (N- C_{ar}), 129.61 (CH_{ar}), 119.45 (CH_{ar}), 112.48 (CH_{ar}). $\text{C}_{14}\text{H}_{14}\text{N}_4$, Calc. 238.12. ESI-MS, (m/z): 239.1 [M^+]. FT-IR(ATR): 3203, 3200 (N-H), 1598 cm^{-1} (C=N).

$\text{N,N}'$ -bis[1-naphthyl]ethane-1,2-diimine, **e**

Compound **e** (Chart 1) was obtained as a green solid from 1-aminonaphthalene (2.0 g, 14 mmol) and aqueous glyoxal (0.9 mL, 7.7 mmol). Yield: 72.5% (1.56 g, 5.06 mmol). M.

p. 245–246 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz): 8.70 (s, 2H, N=CH), 8.36 (t, 2H, $^3J_{\text{H-H}} = 5.04$, CH_{ar}), 8.00 (t, 2H, $^3J_{\text{H-H}} = 4.58$, CH_{ar}), 7.93 (d, 2H, $^3J_{\text{H-H}} = 8.24$, CH_{ar}), 7.61 (m, 6H, CH_{ar}), 7.44 (d, 2H, CH_{ar}). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ in ppm): 161.02 (N=CH), 147.23 (N- C_{ar}), 134.06 (qC_{ar}), 128.81 (CH_{ar}), 128.30 (CH_{ar}), 128.04 (CH_{ar}), 127.20 (CH_{ar}), 126.86 (qC_{ar}), 126.77 (CH_{ar}), 123.74 (CH_{ar}), 113.77 (CH_{ar}). $\text{C}_{22}\text{H}_{16}\text{N}_2$, Calc. 308.13. ESI-MS, (m/z): 309 [M^+]. FT-IR(ATR): 1600 cm^{-1} (C=N).

2.2. General Procedure for the Synthesis of the Complexes

Mechanosynthesis

The α -diimine ligand or its cyclic tautomer precursor **a–e** (1 equiv) and metallic dimeric precursor $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (0.5 equiv) were ground in an agate mortar for 30–45 min at room temperature in air, without the use of a solvent. The resulting complexes were purified by washing with various solvents, as described below.

Synthesis in solution

The corresponding α -diimine ligand or its cyclic tautomer precursor **a–e** (1 mmol) and metallic dimeric precursor $[(\eta^5\text{-Cp}^*)\text{MCl}_2]_2$ (M = Rh or Ir) (0.5 mmol) were dissolved in ethanol (20 mL) in a 50 mL round-bottom flask. The reaction mixture was stirred at room temperature under air for 12 h. Subsequently, the crude product was dried under reduced pressure and purified using different methods, as described below.

$[(\eta^6\text{-}p\text{-cym})\text{Ru(a)Cl}]\text{Cl}$, **1a**

A ground mixture of **a** (39 mg, 0.163 mmol) and $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (50 mg, 0.082 mmol) was washed with cold dichloromethane (5×3 mL) and dried under reduced pressure for 12 h to yield a dark orange solid. Yield: 64 mg, 71.8%. Complex **1a** (Chart 2) only was detected through ESI-MS, $\text{C}_{24}\text{H}_{26}\text{ClN}_2\text{O}_2\text{Ru}$, Calc. 511.07. ESI-MS (m/z): 511.0 [M^+].

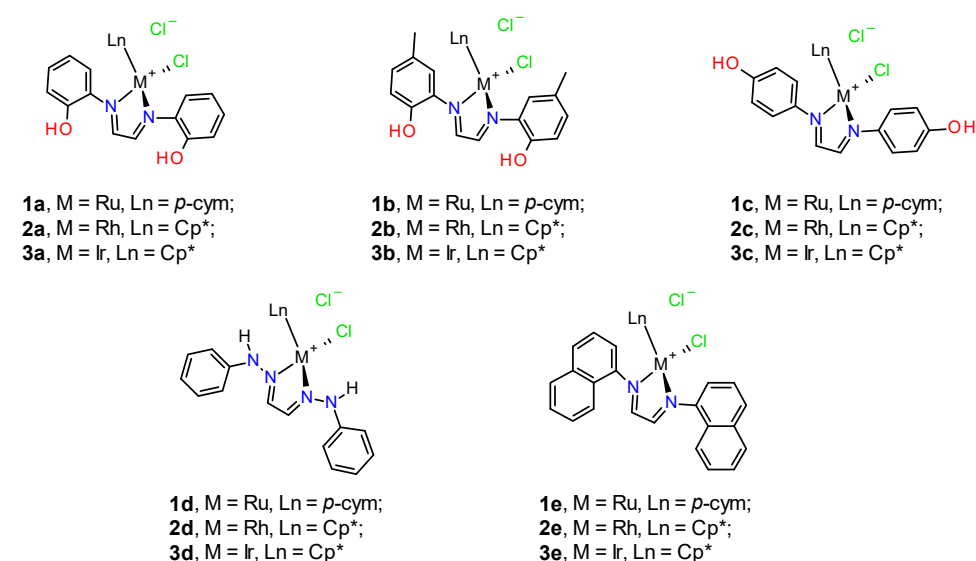


Chart 2. Structures of complexes **1a–e**, **2a–e**, and **3a–e**.

$[(\eta^6\text{-}p\text{-cym})\text{Ru(b)Cl}]\text{Cl}$, **1b**

A ground mixture of **b** (43 mg, 0.163 mmol) and $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (50 mg, 0.082 mmol) was washed with cold dichloromethane (5×3 mL) and hexanes (3×4 mL). The product **1b** (Chart 2) was purified by crystallization with CH_2Cl_2 /hexanes. It was then dried under reduced pressure for 12 h to yield a dark orange solid. Yield: 73 mg, 77.8%. M. p. 217–218 °C. ^1H NMR (CDCl_3 , 750 MHz, δ in ppm, J in Hz): 10.56 (s, 2H, OH), 8.59 (s, 2H, CH=N), 7.57 (s, 2H, CH_{ar}), 7.15 (d, 2H, $^3J_{\text{H-H}} = 8.01$, CH_{ar}), 7.08 (d, 2H, $^3J_{\text{H-H}} = 7.85$, CH_{ar}), 5.44 (d, 2H, $^3J_{\text{H-H}} = 7.8$, $\text{CH}_{p\text{-cym}}$), 5.33 (d, 2H, $^3J_{\text{H-H}} = 7.7$, $\text{CH}_{p\text{-cym}}$), 2.87 (sept, 1H, $^3J_{\text{H-H}} = 5.67$, $\text{CH}_{i\text{Pr}}$), 2.32 (s, 6 H, CH_3), 2.12 (s, 3 H, $\text{CH}_3_{p\text{-cym}}$), 1.10 (d, 6H,

$^3J_{\text{H-H}} = 6.69$, $\text{CH}_3\text{ }i\text{Pr}$). ^{13}C NMR (CDCl_3 , 189 MHz, δ in ppm): 144.7 (N=CH), 139.2 (O- C_{ar}), 131.2 (N- C_{ar}), 128.7 (CH_{ar}), 128.0 (CH_{ar}), 125.9 (CH_{ar}), 125.3 (CH_{ar}), 116.7, (CH_{ar}), 106.9 ($\text{C}_{p\text{-cym}}$), 106.3 ($\text{C}_{p\text{-cym}}$), 88.4 ($\text{CH}_{p\text{-cym}}$), 88.1 ($\text{CH}_{p\text{-cym}}$), 30.4 ($\text{CH }i\text{Pr}$), 21.3 ($\text{CH}_3\text{ }i\text{Pr}$), 18.2 ($\text{CH}_3\text{ }p\text{-cym}$). $\text{C}_{26}\text{H}_{30}\text{ClN}_2\text{O}_2\text{Ru}$, Calc. 539.10 ESI-MS, (m/z): 539.0 [M^+].

$[(\eta^6\text{-}p\text{-cym})\text{Ru}(\text{c})\text{Cl}]\text{Cl}$, **1c**

A ground mixture of **c** (39 mg, 0.163 mmol) and $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (50 mg, 0.082 mmol) was washed with cold dichloromethane (5×3 mL) and hexanes (3×4 mL). The product **1c** (Chart 2) was purified by crystallization with acetone/water. It was then dried under reduced pressure for 12 h to yield a dark orange solid. Yield: 69 mg, 77.9%. M. p. 226–227 °C. The chemical shifts agreed with the data reported in the literature [26]. ^1H NMR ($\text{DMSO-}d_6$, 600 MHz, δ in ppm, J in Hz) 10.48 (s, 2H, OH), 8.47 (s, 2H, N=CH) 7.66 (d, 4H, $^3J_{\text{H-H}} = 8.09$, CH_{ar}), 6.99 (d, 4H, $^3J_{\text{H-H}} = 8.46$, CH_{ar}), 5.50 (d, 2H, $^3J_{\text{H-H}} = 6.48$, $\text{CH}_{p\text{-cym}}$), 5.48 (d, 2H, $^3J_{\text{H-H}} = 6.36$, $\text{CH}_{p\text{-cym}}$), 2.28 (sept, 1H, $^3J_{\text{H-H}} = 6.68$, $\text{CH }i\text{Pr}$), 2.23 (s, 3 H, $\text{CH}_3\text{ }p\text{-cym}$), 0.95 (d, 6H, $^3J_{\text{H-H}} = 7.26$, $\text{CH}_3\text{ }i\text{Pr}$). ^{13}C NMR ($\text{DMSO-}d_6$, 151 MHz, δ in ppm): 163.31 (O- C_{ar}), 160.1 (N=CH), 144.21 (N- C_{ar}), 124.7 (CH_{ar}), 116.1 (CH_{ar}), 106.8 ($\text{C}_{p\text{-cym}}$), 105.9 ($\text{C}_{p\text{-cym}}$), 88.9 ($\text{CH}_{p\text{-cym}}$), 87.2 ($\text{CH}_{p\text{-cym}}$), 30.89 ($\text{CH }i\text{Pr}$), 21.92 ($\text{CH}_3\text{ }i\text{Pr}$), 18.86 ($\text{CH}_3\text{ }p\text{-cym}$). $\text{C}_{24}\text{H}_{26}\text{ClN}_2\text{O}_2\text{Ru}$, Calc. 511.07. ESI-MS, (m/z): 511.0 [M^+]. FT-IR(ATR): 3046 (O-H), 1610 cm^{-1} (C=N).

$[(\eta^6\text{-}p\text{-cym})\text{Ru}(\text{d})\text{Cl}]\text{Cl}$, **1d**

The ground mixture of **d** (39 mg, 0.163 mmol) and $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (50 mg, 0.082 mmol) was washed with cold dichloromethane (5×3 mL) and hexanes (3×4 mL). The product **1d** (Chart 2) was purified by crystallization with CH_2Cl_2 /hexanes. It was then dried under reduced pressure for 12 h to yield a dark orange solid. Yield: 59 mg, 66.3%. M. p. 191–192 °C. ^1H NMR ($\text{DMSO-}d_6$, 750 MHz, δ in ppm, J in Hz): 10.43 (s, 2H, NH), 7.65 (s, 2H, N=CH), 7.27 (t, 4H, $^3J_{\text{H-H}} = 7.34$, CH_{ar}), 6.97 (d, 4H, $^3J_{\text{H-H}} = 8.64$, CH_{ar}), 6.74 (t, 2H, $^3J_{\text{H-H}} = 8.43$, CH_{ar}), 5.81 (d, 2H, $^3J_{\text{H-H}} = 6.18$, $\text{CH}_{p\text{-cym}}$), 5.77 (d, 2H, $^3J_{\text{H-H}} = 6.13$, $\text{CH}_{p\text{-cym}}$), 2.83 (sept, 1H, $^3J_{\text{H-H}} = 6.95$, $\text{CH }i\text{Pr}$), 2.07 (s, 3H, $\text{CH}_3\text{ }p\text{-cym}$), 1.18 (d, 6H, $^3J_{\text{H-H}} = 7.0$, $\text{CH}_3\text{ }i\text{Pr}$). ^{13}C NMR ($\text{DMSO-}d_6$, 189 MHz, δ in ppm): 144.65 (N=CH), 136.63 (CH_{ar}), 129.32 (CH_{ar}), 118.63 (CH_{ar}), 111.66 (CH_{ar}), 106.1 ($\text{C}_{p\text{-cym}}$), 99.8 ($\text{C}_{p\text{-cym}}$), 86.1 ($\text{CH}_{p\text{-cym}}$), 85.3 ($\text{CH}_{p\text{-cym}}$), 29.7 ($\text{CH }i\text{Pr}$), 21.26 ($\text{CH}_3\text{ }i\text{Pr}$), 17.63 ($\text{CH}_3\text{ }p\text{-cym}$). $\text{C}_{24}\text{H}_{28}\text{ClN}_4\text{Ru}$, Calc. 509.10. ESI-MS, (m/z): 509.1 [M^+].

$[(\eta^6\text{-}p\text{-cym})\text{Ru}(\text{e})\text{Cl}]\text{Cl}$, **1e**

The ground mixture of **e** (50 mg, 0.163 mmol) and $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ (50 mg, 0.082 mmol) was washed with cold dichloromethane (5×3 mL) and hexanes (3×4 mL). The product **1e** (Chart 2) was purified by crystallization with CH_2Cl_2 /hexanes. Subsequently, it was dried under reduced pressure for 12 h to yield a dark orange solid. Yield: 84 mg, 84.1%. M. p. 245–246 °C. ^1H NMR ($\text{DMSO-}d_6$, 750 MHz, δ in ppm, J in Hz): 8.90 (s, 2H, N=CH), 8.06 (d, 2H, $^3J_{\text{H-H}} = 8.38$, CH_{ar}), 7.72 (d, 2H, $^3J_{\text{H-H}} = 8.19$, CH_{ar}), 7.39 (t, 2H, $^3J_{\text{H-H}} = 8.32$, CH_{ar}), 7.35 (t, 2H, $^3J_{\text{H-H}} = 8.24$, CH_{ar}), 7.20 (t, 2H, $^3J_{\text{H-H}} = 7.75$, CH_{ar}), 7.08 (d, 2H, $^3J_{\text{H-H}} = 7.90$, CH_{ar}), 6.70 (d, 2H, $^3J_{\text{H-H}} = 7.43$, CH_{ar}), 5.80 (d, 2H, $^3J_{\text{H-H}} = 6.26$, $\text{CH}_{p\text{-cym}}$), 5.76 (d, 2H, $^3J_{\text{H-H}} = 6.17$, $\text{CH}_{p\text{-cym}}$), 2.83 (sept, 1H, $^3J_{\text{H-H}} = 6.66$, $\text{CH }i\text{Pr}$), 2.08 (s, 3H, $\text{CH}_3\text{ }p\text{-cym}$), 1.16 (d, 6H, $^3J_{\text{H-H}} = 7.02$, $\text{CH}_3\text{ }i\text{Pr}$). ^{13}C NMR ($\text{DMSO-}d_6$, 189 MHz, δ in ppm): 144.5 (N=CH), 134.5 (N- C_{ar}), 129.0 (C_{ar}), 127.9 (CH_{ar}), 126.8 (CH_{ar}), 125.7 (CH_{ar}), 123.9 (C_{ar}), 123.0 (CH_{ar}), 122.5 (CH_{ar}), 115.8 (CH_{ar}), 100.2 (CH_{ar}), 107.9 ($\text{C}_{p\text{-cym}}$), 106.6 ($\text{C}_{p\text{-cym}}$), 86.6 ($\text{CH}_{p\text{-cym}}$), 85.7 ($\text{CH}_{p\text{-cym}}$), 30.2 ($\text{CH }i\text{Pr}$), 21.7 ($\text{CH}_3\text{ }i\text{Pr}$), 18.1 ($\text{CH}_3\text{ }p\text{-cym}$). $\text{C}_{32}\text{H}_{30}\text{ClN}_2\text{Ru}$, Calc. 579.11. ESI-MS, (m/z): 579.1 [M^+]. FT-IR(ATR): 1605 cm^{-1} (C=N).

$[(\eta^5\text{-Cp}^*)\text{Rh}(\text{a})\text{Cl}]\text{Cl}$, **2a**

The reaction product of ligand **a** (39 mg, 0.162 mmol) and dimer $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ (50 mg, 0.081 mmol) was dissolved in dichloromethane (5 mL), and hexane (10 mL) was added to yield a solid, which was filtered and washed with the same mixture of solvents.

Finally, the solid was dried for 12 h under reduced pressure to obtain a dark red solid, corresponding to **2a** (Chart 2). Yield: 66 mg, 74.3%. M. p. 203–204 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz): 7.29 (s, 2H), 6.74 (t, 2H, $^3J_{\text{H-H}} = 8.72$, CH_{ar}), 6.69 (d, 2H, $^3J_{\text{H-H}} = 8.14$, CH_{ar}), 6.63 (d, 2H, $^3J_{\text{H-H}} = 8.24$, CH_{ar}), 6.60 (t, 2H, $^3J_{\text{H-H}} = 7.98$, CH_{ar}), 5.26 (s, 2H), 1.62 (s, 15H, CH_3 Cp*). ^{13}C NMR (189 MHz, DMSO- D_6) δ 141.02 (C=N), 129.88 (N- C_{ar}), 121.1 (CH_{ar}), 118.4 (CH_{ar}), 115.8 (CH_{ar}), 113.91 (CH_{ar}), 98.57 (d, $^1J_{\text{C-Rh}} = 7.48$, C_{Cp^*}), 75.01, 8.34 (CH_3 Cp*). $\text{C}_{24}\text{H}_{27}\text{ClN}_2\text{O}_2\text{Rh}$, Calc. 513.09. ESI-MS, (m/z): 513.0 [M^+].

$[(\eta^5\text{-Cp}^*)\text{Rh(b)Cl}]\text{Cl}$, **2b**

The reaction product of ligand **b** (43 mg, 0.162 mmol) and dimer $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ (50 mg, 0.081 mmol) was dissolved in dichloromethane (5 mL), and hexane (10 mL) was added to yield a solid. The solid was filtered and washed with the same mixture of solvents. Finally, the solid was dried for 12 h under reduced pressure to obtain a brownish-red solid, corresponding to **2b** (Chart 2). Yield: 70 mg, 75.3%. M. p. 201–202 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz): 7.17 (s, 2H), 6.50 (d, 2H, $^3J_{\text{H-H}} = 8.92$, CH_{ar}), 6.48 (s, 2H, CH_{ar}), 6.40 (d, 2H, $^3J_{\text{H-H}} = 8.17$, CH_{ar}), 5.17 (s, 2H), 2.14 (s, 6H, CH_3) 1.62 (s, 15H, CH_3 Cp*). ^{13}C NMR (189 MHz, DMSO- D_6) δ 138.7 (C=N), 129.7 (N- C_{ar}), 129.5 (CH_{ar}), 118.6 (CH_{ar}), 115.4 (CH_{ar}), 114.24 (CH_{ar}), 98.4 (d, $^1J_{\text{C-Rh}} = 7.50$, C_{Cp^*}), 74.98, 20.14 (CH_3), 8.22 (CH_3 Cp*). $\text{C}_{26}\text{H}_{31}\text{ClN}_2\text{O}_2\text{Rh}$, Calc. 541.11. ESI-MS, (m/z): 541.0 [M^+].

$[(\eta^5\text{-Cp}^*)\text{Rh(c)Cl}]\text{Cl}$, **2c**

The reaction product of ligand **c** (43 mg, 0.162 mmol) and dimer $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ (50 mg, 0.081 mmol) was washed with dichloromethane, and then dissolved and extracted using ethanol, which was eliminated under reduced pressure. Finally, the solid was dried for 12 h to obtain a deep red solid, corresponding to **2c** (Chart 2). Yield: 70 mg, 79.0%. M. p. 219–220 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz) 10.46 (s, 2H, OH), 8.46 (s, 2H, N=CH) 7.61 (d, 4H, $^3J_{\text{H-H}} = 8.09$, CH_{ar}), 7.00 (d, 4H, $^3J_{\text{H-H}} = 8.16$, CH_{ar}), 1.22 (s, 15 H, CH_3 Cp*). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ in ppm): 162.8 (N=CH), 159.8 (O- C_{ar}), 140.3 (N- C_{ar}), 124.5 (CH_{ar}), 116.0 (CH_{ar}), 97.9 (d, $^1J_{\text{C-Rh}} = 5.30$, C_{Cp^*}), 8.37 (CH_3 Cp*). $\text{C}_{24}\text{H}_{27}\text{ClN}_2\text{O}_2\text{Rh}$, Calc. 513.09. ESI-MS, (m/z): 513.0 [M^+]. FT-IR(ATR): 3019 (O-H), 1605 cm^{-1} (C=N).

$[(\eta^5\text{-Cp}^*)\text{Rh(e)Cl}]\text{Cl}$, **2e**

The reaction product of ligand **e** (50 mg, 0.162 mmol) and dimer $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ (50 mg, 0.081 mmol) was dissolved in dichloromethane (5 mL), and hexane (10 mL) was added to yield a solid. The solid was filtered and washed with the same mixture of solvents. Finally, the solid was dried for 12 h under reduced pressure to obtain a dark red solid, corresponding to **2e** (Chart 2). Yield: 76 mg, 76.0%. M. p. 243–244 °C. ^1H NMR (DMSO- d_6 , 750 MHz, δ in ppm, J in Hz) 8.69 (s, 2H, CH=N), 8.04 (d, 2H, $^3J_{\text{H-H}} = 7.17$, CH_{ar}), 7.70 (d, 2H, $^3J_{\text{H-H}} = 8.13$, CH_{ar}), 7.39 (t, 2H, $^3J_{\text{H-H}} = 8.08$, CH_{ar}), 7.34 (t, 2H, $^3J_{\text{H-H}} = 8.10$, CH_{ar}), 7.18 (t, 2H, $^3J_{\text{H-H}} = 7.72$, CH_{ar}), 7.06 (d, 2H, $^3J_{\text{H-H}} = 7.98$, CH_{ar}), 6.66 (d, 2H, $^3J_{\text{H-H}} = 7.46$, CH_{ar}), 1.61 (s, 15 H, CH_3 Cp*). ^{13}C NMR (DMSO- d_6 , 189 MHz, δ in ppm): 161.0 (N=CH), 147.2 (N- C_{ar}), 134.6, 128.2, 128.0 (CH_{ar}), 127.2 (CH_{ar}), 126.9 (CH_{ar}), 126.8 (CH_{ar}), 126.7 (CH_{ar}), 126.0 (CH_{ar}), 113.8 (CH_{ar}), 99.2 (d, $^1J_{\text{C-Rh}} = 7.6$, C_{Cp^*}), 9.04 (CH_3 Cp*). $\text{C}_{32}\text{H}_{31}\text{ClN}_2\text{Rh}$, Calc. 581.12. ESI-MS, (m/z): 581.0 [M^+]. FT-IR(ATR): 1593 cm^{-1} (C=N).

$[(\eta^5\text{-Cp}^*)\text{Ir(a)Cl}]\text{Cl}$, **3a**

The reaction product of ligand **a** (30 mg, 0.125 mmol) and dimer $[(\eta^5\text{-Cp}^*)\text{IrCl}_2]_2$ (50 mg, 0.063 mmol) was sonicated for 20 min with 20 mL of a 1:1 mixture of ethyl acetate and hexane. Subsequently, the solid product was filtered and washed with the same mixture of solvents. Finally, the solid was dried for 12 h under reduced pressure to obtain a dark green solid, corresponding to **3a** (Chart 2). Yield: 64 mg, 79.3%. M. p. 208–209 °C. ^1H NMR (CDCl_3 , 400 MHz, δ in ppm): 8.75 (s, 2H, N-CH), 7.71–6.73 (m, 8H, CH), 1.34 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (CDCl_3 , 100 MHz, δ in ppm): 169.23 (C=N), 150.12 (C-OH),

136.19–119.26 (C_6H_4), 92.93 ($C_5(CH_3)_5$) y 9.41 ($C_5(CH_3)_5$). $C_{24}H_{27}ClIrN_2O_2$, Calc. 603.14. ESI-MS (m/z): 603.2 [M^+]. FT-IR(ATR): 3451 (O–H), 1600 cm^{-1} (C=N).

$[(\eta^5-Cp^*)Ir(b)Cl]Cl$, **3b**

The reaction product of ligand **b** (34 mg, 0.125 mmol) and dimer $[(\eta^5-Cp^*)IrCl_2]_2$ (50 mg, 0.063 mmol) was sonicated for 20 min using 10 mL dichloromethane, yielding a black solid. The solid was filtered and washed with dichloromethane (5×2 mL) and hexanes (5×2 mL). Finally, the solid was dried for 12 h under reduced pressure to obtain a black crystalline solid, corresponding to **3b** (Chart 2). Yield: 62 mg, 73.9%. M. p. 210–211 °C. ^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 9.0 (s, 2H, N–CH), 7.5–7.0 (m, 4H, CH_{ar}), 7.25 (s, 2H, CH_{ar}), 2.43 (s, 6H, CH_3), 1.47 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ in ppm): 168.29 (C=N), 147.07 (C–OH), 135.14–118.37 (C_6H_3), 92.24 ($C_5(CH_3)_5$) y 7.88 ($C_5(CH_3)_5$), 20.16 (CH_3). $C_{26}H_{31}ClIrN_2O_2$, Calc. 631.17 ESI-MS (m/z): 631.2 [M^+]. FT-IR(ATR): 1615 cm^{-1} (C=N).

$[(\eta^5-Cp^*)Ir(c)Cl]Cl$, **3c**

The reaction product of ligand **c** (30 mg, 0.125 mmol) and dimer $[(\eta^5-Cp^*)IrCl_2]_2$ (50 mg, 0.063 mmol) was sonicated for 20 min with 10 mL of a 2:1 mixture of dichloromethane and hexane. Thereafter, the solid product was filtered and washed with cold dichloromethane (5×2 mL) and hexanes (5×2 mL). Finally, the solid was dried for 12 h under reduced pressure to obtain a black solid, corresponding to **3c** (Chart 2). Yield: 65 mg, 81.4%. M. p. 215–216 °C. ^1H NMR ($DMSO-d_6$, 400 MHz, δ in ppm): 10.5 (s, 2H, OH), 9.03 (s, 2H, N–CH), 7.69–6.74 (dd, 8H, CH_{ar}), 1.34 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($DMSO-d_6$, 100 MHz, δ in ppm): 165.16 (C=N), 159.86 (C–OH), 140.68–115.93 (C_6H_4), 91.58 $C_5(CH_3)_5$ y 8.09 $C_5(CH_3)_5$. $C_{24}H_{27}ClIrN_2O_2$, Calc. 603.14. ESI-MS (m/z): 603.2 [M^+]. FT-IR(ATR): 3056 (O–H), 1603 cm^{-1} (C=N).

$[(\eta^5-Cp^*)Ir(d)Cl]Cl$, **3d**

The reaction product of ligand **d** (30 mg, 0.125 mmol) and dimer $[(\eta^5-Cp^*)IrCl_2]_2$ (50 mg, 0.063 mmol) was dissolved in a small amount of dichloromethane (1 mL), and hexanes (20 mL) were added to yield a dark red solid. The product was recrystallized again using the same solvents and dried for 12 h under reduced pressure to obtain a brown solid, corresponding to **3d** (Chart 2). Yield: 63 mg, 79.4%. M. p. 220–221 °C. ^1H NMR ($DMSO-d_6$, 400 MHz, δ in ppm): 10.49 (s, 2H, NH), 7.74 (s, 2H, N–CH), 7.32–6.55 (m, 10H, CH_{ar}), 1.7 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (d_6 -DMSO, 100 MHz, δ in ppm): 145.35 (C=N), 136.83–111.88 (C_6H_5), 92.04 $C_5(CH_3)_5$ y 8.20 $C_5(CH_3)_5$. $C_{24}H_{29}ClIrN_4$, Calc. 601.17. ESI-MS (m/z): 601.0 [M^+]. FT-IR(ATR): 1605 cm^{-1} (C=N).

$[(\eta^5-Cp^*)Ir(e)Cl]Cl$, **3e**

The reaction product of ligand **e** (38 mg, 0.125 mmol) and dimer $[(\eta^5-Cp^*)IrCl_2]_2$ (50 mg, 0.063 mmol) was dissolved in dichloromethane (5 mL), and then hexanes (20 mL) were added to yield a solid. The product was filtered, washed with the same mixture of solvents, and dried for 12 h under reduced pressure to obtain a dark green solid, corresponding to **3e** (Chart 2). Yield: 74.5, 84.0%. M. p. 252–253 °C. ^1H NMR ($DMSO-d_6$, 750 MHz, δ in ppm, J in Hz) 9.56 (s, 2H, CH=N), 8.49 (t, 2H, $^3J_{H-H} = 7.40$, CH_{ar}), 8.17–8.14 (m, 6H, CH_{ar}), 8.07 (d, 2H, $^3J_{H-H} = 8.13$, CH_{ar}), 7.80–7.78 (m, 4H, CH_{ar}), 0.93 (s, 15H, CH_3 Cp^*). ^{13}C NMR ($DMSO-d_6$, 189 MHz, δ in ppm): 172.8 (N=CH), 145.9 (N- C_{ar}), 133.8, 129.9, 129.1 (CH_{ar}), 128.7 (CH_{ar}), 127.8 (CH_{ar}), 126.6 (CH_{ar}), 125.7 (CH_{ar}), 123.1 (CH_{ar}), 119.2 (CH_{ar}), 92.6 (C_{Cp^*}), 8.3 (CH_3 Cp^*). $C_{32}H_{31}ClIrN_2$, Calc. 671.17, ESI-MS, (m/z): 671.2 [M^+].

2.3. General Procedure for FA Decomposition in Aqueous Media

In a 5 mL reactor vial, water (2 mL), FA (2.65 mmol), and the catalytic precursor (2.65×10^{-3} mmol) were added in air. The reaction mixture was placed in a Monowave 50 synthesis reactor (Anton Paar®) and heated at 110 °C for the duration of the reaction.

Residual FA was quantified through titration with sodium hydroxide (0.1 M) and phenolphthalein (1%) as an indicator. Measurements were performed in triplicate to determine the average and standard deviation.

2.4. General Procedure for the Evolution of H₂ and CO₂ Gases via FA Decomposition in Aqueous Media

In a 50 mL Schlenk tube connected to a graduated bottle, water (2 mL), formic acid (2.65 mmol), and the catalytic precursor (2.65×10^{-3} mmol) were added in air. The catalytic mixture was maintained at 90 °C for the duration of the reaction, and gas evolution was measured in a graduated bottle and compared with the theoretical volume (ideal gas equation $n = PV/RT$). Measurements were performed in triplicate to determine the average and standard deviation.

2.5. Catalyst Reusability Test in FA Decomposition

The catalytic precursor **3d**, [Ir] = 0.1 mol% (1.2 mg **3d** in 10 mL water or 1.2 mg/10 mL, 2417.0 µL, 0.29 mg) was placed in a 50 mL Schlenk tube connected to a graduated bottle, and formic acid was added (four successive additions of 0.457 mmol). The reaction was conducted at 80 °C throughout the duration required for each addition of the substrate.

2.6. General Procedure for the Hydrogenation of Carbon Dioxide

The CO₂ hydrogenation reactions were performed in a Parr[®] stainless-steel high-pressure reactor equipped with a 6 mL container and a magnetic stir bar. The precatalyst (5 µmol) was dissolved in a solvent mixture (H₂O:THF 1:2), and 1 mL of NEt₃ (7.17 mmol) was added to the container. The reactor was purged with nitrogen gas for 2 min and CO₂ was charged to 20 bar, followed by hydrogen until a total pressure of 60 bar was reached. The reaction mixture was placed at 500 rpm and 110 °C for the designated reaction time. Upon completion, the reactor was cooled to room temperature and carefully depressurized to an internal pressure of 0 bar. *N,N*-dimethylformamide (DMF) was added to the resulting solution as an internal standard (132 µL, 1.7 mmol). An aliquot (100 µL) of this solution was collected in an NMR tube, and 0.5 mL of D₂O was added for analysis through ¹H NMR spectroscopy. Measurements were performed in triplicate to determine the average and standard deviation.

2.7. Catalyst Reusability Test in CO₂ Hydrogenation

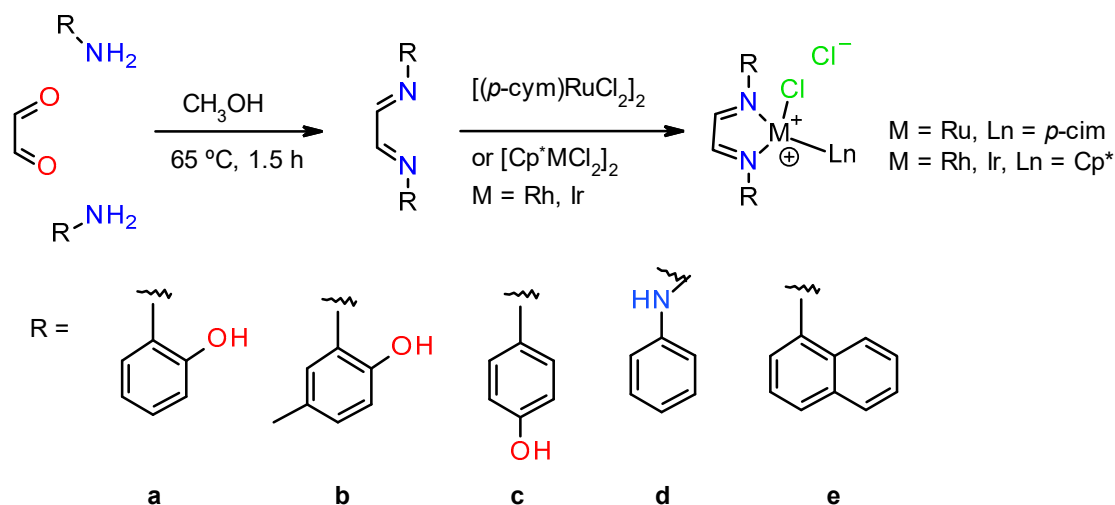
The catalytic precursor **1e** (5 µmol) was dissolved in the solvent mixture (H₂O:THF 1:2, 2 mL), and 1 mL of NEt₃ (7.17 mmol) was added to the container. The conditions were established as mentioned above. After 20 h, when the reactor had cooled and depressurized, an aliquot (100 µL) of this solution was collected in an NMR tube, and 3.5 µL of DMF and 0.5 mL of D₂O were added for analysis through ¹H NMR spectroscopy. The reactor was refilled with NEt₃ and the solvent mixture, repeating the cycle three more times.

3. Results and Discussion

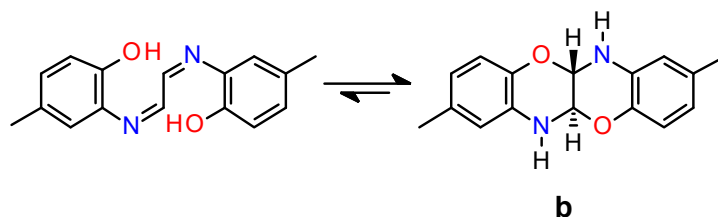
3.1. Synthesis and Characterization of Ligands and Complexes

Ligands or their cyclic tautomer precursors **a–e** (Scheme 1) were synthesized via condensation of glyoxal with two equivalents of aromatic primary amines, following the method reported by Sawama et al. [34] Compounds **a** [32], **c** [26], and **d** [33] have been previously reported, including NMR characterization consistent with this study; compounds **b** and **e** are newly reported herein. Notably, compound **b** undergoes cyclic tautomerization (Scheme 2), previously observed for compound **a** [35], which shows typical chemical shifts in the ¹H and ¹³C NMR spectra; for example, the NH and aliphatic CH hydrogens resonate at $\delta = 7.25$ and 5.25 ppm, respectively, appearing as doublets because

of the coupling between them. The sp^3 carbon in the CH group is observed at $\delta = 75.8$ ppm, and the aromatic carbons bound to oxygen and nitrogen appear at $\delta = 139.6$ and 130.5 ppm, respectively, which confirms the proposed cyclic form.



Scheme 1. Synthesis of compounds **a–e**, ruthenium(II) (**1b–1e**), rhodium(III) (**2a–2c**, **2e**), and iridium(III) complexes (**3a–3e**).



Scheme 2. Cyclic tautomerization of ligand **b**.

Complexes were synthesized from the dimeric metal precursors $[(\eta^6\text{-}p\text{-cym})\text{RuCl}_2]_2$ ($p\text{-cym} = p\text{-cymene}$) or $[(\eta^5\text{-Cp}^*)\text{MCl}_2]_2$ ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$, $\text{M} = \text{Rh, Ir}$), and the corresponding ligands **a–e** were successfully obtained for 13 of them (**1b–1e**, **2a–2c**, **2e**, and **3a–3e**) (Scheme 1). Complex **1a** was only detected through ESI-MS ($[\text{M}]^+ = 511.0$ m/z), but could not be isolated and characterized; there was evidence regarding its rapid decomposition. Meanwhile, complex **2d** could not be synthesized, and there was no evidence of its formation. Complex **1c** has been previously reported with nitrate as the counterion [26].

In all complexes reported here, the most characteristic signal in the ^1H NMR spectra corresponds to the hydrogen of the CH group in the imine fragment, which is shifted to low frequencies, showing a clear trend. The complexes containing $-\text{OH}$ groups show this signal at approximately $\delta = 9.21$ to 8.46 ppm, while in the complexes containing $-\text{NH}$ groups, the imine CH resonates at $\delta = 7.65$ to 7.58 ppm. The acidic hydrogens in the $-\text{OH}$ group are observed at $\delta 10.96$ to 10.46 ppm and $-\text{NH}$ at $\delta 10.85$ to 10.38 ppm. The complexes with ligands derived from naphthylamine show the imine CH signal at $\delta = 9.56$ to 8.69 ppm.

On the other hand, in the ^{13}C NMR spectra, the carbon of the CH group in the imine fragment is most shifted to low frequencies, showing a signal at $\delta = 172.8$ to 144.5 ppm. The other signals in the ^{13}C NMR spectra are consistent with aromatic CH or quaternary carbons.

Representative examples of ^1H and ^{13}C NMR spectra for **1b**, **2c**, **3a**, and **3e** complexes are shown in the electronic Supporting Information.

Ligands and complexes were studied using ESI-MS. In the mass histogram of ligands **a–e**, molecular ions $[\text{M}]^+$ were observed in all cases. Additionally, ligand **a** showed an association of two water molecules with two molecules of the compound $[2\text{M}\cdot 2\text{H}_2\text{O}]^+$ at

$m/z = 516$. In the ESI-MS spectra of complexes **1a–1e**, **2a–2c**, **2e**, and **3a–3e**, molecular ions $[M]^+$ were observed in all cases. Additionally, some of them showed ion peaks resulting from the fragmentation of the chloro ligand $[M-Cl]^+$, for example, complexes **1b**, **1d**, **2b**, **3a**, **3b**, and **3d**.

The compounds were analyzed by DSC to determine the degree of purity, as well as the decomposition temperature, to ensure that the catalytic test temperatures did not degrade the precatalysts. The analysis of the DSC curves allowed for determining a decomposition temperature range of 210–235 °C for Ru complexes, 185–245 °C for Rh complexes, and 215–240 °C for Ir complexes (Supporting Information).

The complexes **1d**, **3a**, and **3c** were studied using single-crystal X-ray diffraction (XRD). The structure of **1d** (orthorhombic, $Pbca$), crystallized from acetone/water, is presented in Figure 1. A spatial orientation of the i Pr group of p -cymene is observed toward the α -diimine ligand, and the methyl group of p -cymene is observed toward the chloro ligand. The geometry around the ruthenium atom is pseudo-octahedral, with the two nitrogen atoms of the α -diimine, a chloro ligand, and three positions occupied by the p -cymene ligand. The crystal structure shows an intermolecular hydrogen bond between the $-NH-$ and the chloride with a 3.133 Å distance.

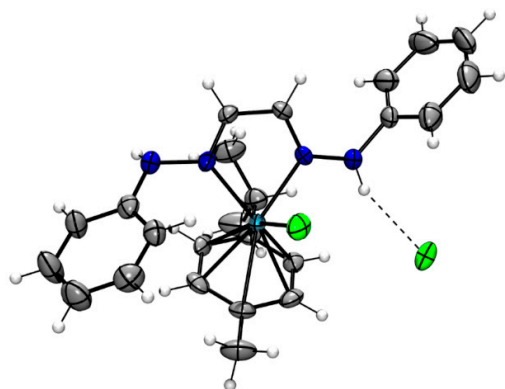


Figure 1. Crystal structure for complex **1d**, orthorhombic, $Pbca$.

Complex **3a** (monoclinic, $C2/c$) was crystallized in water and studied via single-crystal XRD. Figure 2 shows that the geometry around the iridium atom is pseudo-octahedral, with coordination by two nitrogen atoms from the α -diimine, one chloro ligand, and three positions occupied by the Cp^* ligand. Hydrogen bonds are observed between the chloride and the o -OH group at the α -diimine ligand (3.107 Å), as well as between the oxygen atom of the crystallization water molecule and the other o -OH group on the α -diimine ligand (2.652 Å).

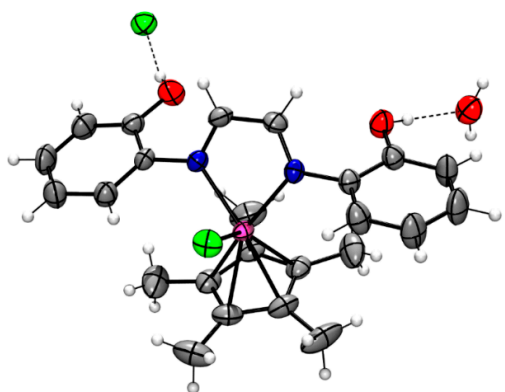


Figure 2. Crystal structure for complex **3a**, monoclinic, $C2/c$.

Complex **3c** (monoclinic, $P2_1/c$) was crystallized from acetone/water, and the structure is shown in Figure 3. It reveals that the geometry around the iridium atom is pseudo-octahedral, with two nitrogen atoms from the α -diimine, one chloro ligand, and three positions occupied by the Cp^* ligand. A hydrogen bond is observed between the chloro anion and the p -OH groups on the α -diimine ligand (3.019 Å).

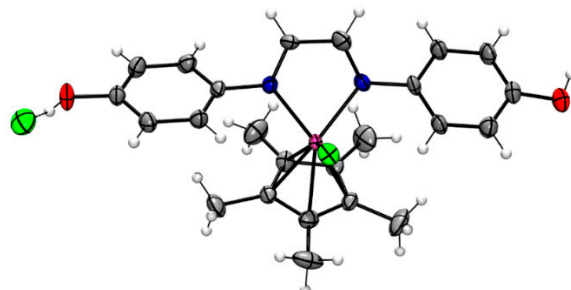
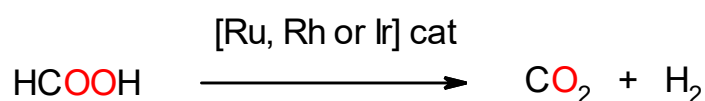


Figure 3. Crystal structure for complex **3c**, monoclinic, $P2_1/c$.

3.2. Catalytic Activity in FA Decomposition Using Complexes as Precatalysts

The incorporation of α -diimine ligands with protic groups improved the solubility in water of the ruthenium (**1b–1e**), rhodium (**2a–2c**, **2e**), and iridium (**3a–3e**) complexes, enabling the dehydrogenation of FA in aqueous medium; this process involves the generation of gaseous H_2 and CO_2 (Scheme 3). For this reaction, a Monowave-50 synthesis reactor was used, which allows continuous pressure monitoring of the system to be observed.



Scheme 3. Catalytic decomposition of formic acid to hydrogen and CO_2 .

FA dehydrogenation was initiated with the most stable iridium complexes (**3a–3e**) as precatalysts (0.1 mol%) in an aqueous medium. Figure 4 shows the evolution of pressure vs. time for the iridium complexes. The increase in system pressure can be attributed to the presence of the H_2 and CO_2 generated.

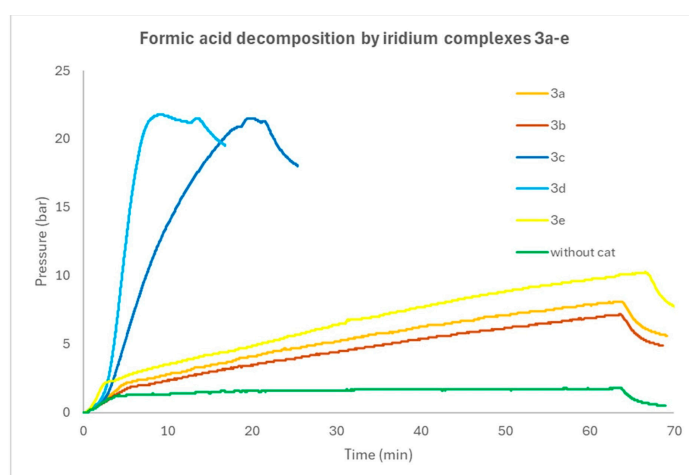


Figure 4. FA decomposition to H_2 and CO_2 , using 0.1 mol% of iridium complexes (**3a–3e**) as precatalysts in aqueous media.

An experiment was conducted without a catalytic precursor (Figure 4, green curve) to rule out the possibility of spontaneous formic acid decomposition under the reaction

conditions. No change in system pressure was observed, indicating that the reaction did not proceed without a catalytic precursor.

Complexes **3c** and **3d** exhibited the best catalytic performance in the dehydrogenation of FA in aqueous medium (Figure 4, navy-blue and light-blue curves), reaching the maximum pressure within a short reaction time in the synthesis reactor.

A previous report [36] demonstrated that the optimal pH for HCOOH dehydrogenation in water is 1.4. The complexes used in that work showed a higher catalytic performance under these conditions compared to catalysis performed at a higher pH (pH = 3.7 using a 1:1 mixture of [HCOOH]/[HCOONa]). Based on these findings, we measured the initial pH of all catalytic solutions and found an initial pH of 1.4, which increased to 5 after the catalytic reaction. These pH changes were even more noticeable for complexes **3c** and **3d**, correlating with greater substrate consumption.

Following these observations, we focused on the catalytic study of this reaction with complex **3c** and conducted several experiments using reduced precatalyst loadings (Table 1, entries 1 to 3), as well as using silver trifluoromethanesulfonate (AgOTf) (entry 4) in an equimolar amount with respect to the complex. The conversions of H₂ and CO₂ were determined by the titration of residual HCOOH using 0.1 M NaOH.

Table 1. Dehydrogenation of FA with **3c** complex as a precatalyst.

Entry	[3c] (mmol)	[HCOOH] _{residual} (mmol)	Conversion (%)
1	2.82×10^{-3}	0.0821	96.9
2	2.82×10^{-4}	1.1530	56.5
3	2.82×10^{-5}	2.65	0
4 ^a	2.82×10^{-4}	0.9059	65.8

Conditions: HCOOH (2.65 mmol), solvent: H₂O (2 mL), 110 °C, 1 h. The residual HCOOH was determined by titration with NaOH. ^a AgOTf (2.82×10^{-4} mmol) was added to the precatalyst solution.

When the precatalyst load was reduced from 2.82 μmol (entry 1) to 0.282 μmol (entry 2), the conversion of the reaction dropped by almost half, and a further decrease resulted in zero conversion (entry 3). Conversely, the addition of AgOTf to complex **3c** resulted in a slight increase in conversion (entry 4).

Based on the previous results, we decided to study the decomposition of FA to H₂ and CO₂ using the remaining prepared complexes as recatalysts at a load of 2.65 μmol, HCOOH (2.65 mmol), water as a solvent (2 mL), and a temperature of 110 °C (Monowave 50). The conversions of H₂ and CO₂ were determined by the titration of residual HCOOH with 0.1 M NaOH. The results are presented in Table 2. In comparing the catalytic activity of all the synthesized compounds, we observed that the iridium complexes (entries 1 to 6) were the most efficient precatalysts for this reaction, followed by the rhodium complexes (entries 7 to 10), and finally the ruthenium complexes (entries 11 to 14). In all cases, the complexes with α-diimines derived from *p*-aminophenol (**1c**, **2c**, and **3c**) and phenyl hydrazine (**1d**, **2d**, and **3d**) were the most effective in each series. The **3d** complex (entry 5) presented the highest values of TON (1980.5) and TOF (3203.3 h^{−1}) within a short reaction time.

Table 2. Decomposition of FA to H₂ and CO₂ by ruthenium, rhodium, and iridium complexes as precatalysts.

Entry	Complex	Time (min)	[H ₂] (mmol)	Conversion (%)	TON	TOF (h ^{−1})
1	3a	55	1.88 ± 0.11	70.93	1416.1	1519.8
2	3b	57	1.68 ± 0.09	64.65	1350.7	1264.4
3	3c	55	2.62 ± 0.01	98.94	1975.4	1835.2
4 ^a	3c	60	2.62 ± 0.01	98.82	1973.8	1973.8
5	3d	32	2.62 ± 0.01	99.53	1980.5	3203.2

Table 2. Cont.

Entry	Complex	Time (min)	[H ₂] (mmol)	Conversion (%)	TON	TOF (h ^{−1})
6 ^b	3e	60	0.44 ± 0.05	16.25	192.53	192.4
7	2a	51	1.60 ± 0.09	59.60	1186.0	1379.9
8	2b	55	1.79 ± 0.08	66.12	1315.6	1383.0
9	2c	55	2.08 ± 0.06	75.98	1511.9	1645.6
10	2e	60	1.43 ± 0.10	54.08	1076.1	1076.8
11	1b	62	0.42 ± 0.24	15.90	283.80	274.7
12	1c	60	0.85 ± 0.17	28.64	484.6	484.6
13	1d	64	0.79 ± 0.32	29.73	503.0	470.4
14	1e	64	0.49 ± 0.12	17.82	301.5	281.4

Conditions: HCOOH (2.65 mmol), complex = precatalyst (2.65 μmol), solvent: H₂O (2 mL), temperature = 110 °C (Monowave 50). The conversion of H₂ was determined by the titration of residual HCOOH with NaOH 0.1 M. TON = (mmol of formate/mmol of precatalyst). TOF = TON/reaction time (h). ^a With a drop of Hg. ^b Measured with precatalyst = 5 μmol.

To verify that the catalytic reaction was carried out in a homogeneous phase by the complexes and to exclude the action of nanoparticles, an experiment was conducted with a drop of mercury (Table 2, entry 4) added to complex 3c, resulting in a slight decrease in conversion.

Additionally, an experiment was conducted to recycle the catalytic precursor at 80 °C under an open atmosphere. The progress of the reaction was monitored by collecting the evolved gases over water. Specifically, we employed the method reported by Fujita [37], in which H₂ was collected during the oxidative dehydrogenation process of alcohols. The experiment involved four additions of substrate to a fixed amount of catalytic precursor (0.1 mol%). The results indicated that precatalyst 3d exhibited a good catalytic performance over 210 min (Figure 5), after which substrate conversion decreased and proceeded slower. This trend is consistent with that reported in the literature, which suggests degradation of the active species over extended reaction times.

FA decomposition to yield H₂ and CO₂ was studied under similar conditions by collecting the evolved gases over water. The ruthenium (1b–1e), rhodium (2a–2c, 2e), and iridium (3a–3e) complexes were employed as precatalysts at a loading of 2.65 μmol, with HCOOH (2.65 mmol) and water as a solvent (2 mL) at 90 °C. Reaction times were recorded until the 100% conversion of formic acid. The results presented in Table 3 are consistent with those given in the previous table (Table 2), confirming that iridium complexes 3d (entry 4) (TON = 2150.2, TOF = 3861.8 h^{−1}) and 3c (entry 3) (TON = 2013.5, TOF = 1611.3 h^{−1}) are the most efficient precatalysts for this reaction.

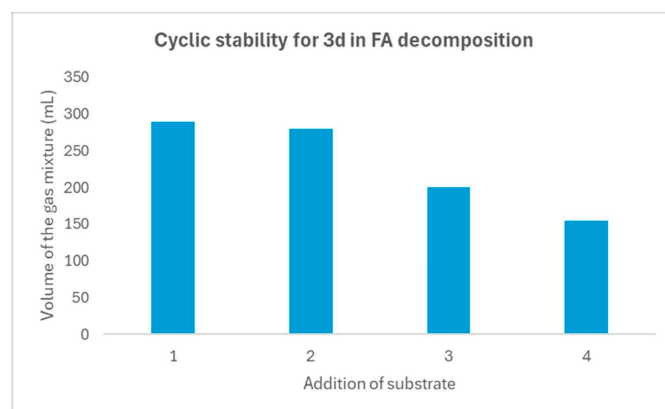


Figure 5. Cyclic stability in FA decomposition, using 3d as precatalyst. Reaction time: 20, 30, 65, and 95 min. Conditions: 80 °C, [Ir] 0.1 mol%, and four additions of HCOOH (20.0 μL, 0.457 mmol). The volume of the gas mixture was measured via water displacement.

Table 3. FA decomposition to yield H₂ and CO₂ using ruthenium, rhodium, and iridium complexes as precatalysts.

Entry	Complex	Time (min)	[H ₂] (mmol)	Conversion (%)	TON	TOF (h ^{−1})
1	3a	56	4.02 ± 0.28	75.8	1513.9	1624.6
2	3b	68	3.67 ± 1.74	69.1	1445.6	1266.9
3	3c	75	5.34 ± 2.18	100.0	2013.5	1611.3
4	3d	33	5.72 ± 0.12	100.0	2150.2	3861.8
5 ^a	3e	60	0.93 ± 1.40	17.7	209.6	211.7
6	2a	45	3.16 ± 0.07	59.7	1188.2	1584.3
7	2b	57	3.67 ± 0.17	69.1	1376.9	1521.5
8	2c	52	3.85 ± 0.08	72.5	1444.7	1713.7
9	2e	63	2.96 ± 0.17	55.9	1112.8	1089.1
10	1b	66	0.95 ± 0.44	18.0	321.4	293.4
11	1c	60	1.40 ± 0.23	26.5	449.0	449.0
12	1d	69	1.55 ± 0.06	29.4	497.1	430.2
13	1e	68	0.87 ± 0.12	16.4	277.9	245.3

Conditions: HCOOH (2.65 mmol), complex = precatalyst (2.65 μmol), solvent: H₂O (2 mL), and temperature = 90 °C. The conversions of H₂ and CO₂ were determined by measuring the gas mixture via water displacement. TON = (mmol of formate/mmol of precatalyst). TOF = TON/reaction time (h). ^a Measured at precatalyst load = 5 μmol.

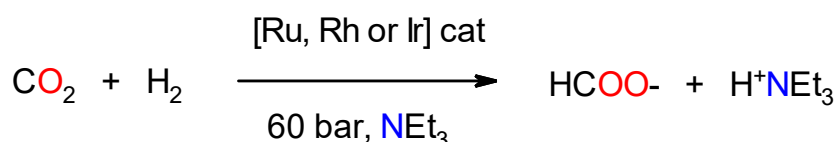
The initial goal of this work was demonstrated with iridium complexes **3d** and **3c**, containing the –NH– and –OH protic groups as efficient precatalysts for this reaction; however, they can be compared with other ruthenium and iridium complexes reported in the literature, as shown in Table 4.

Table 4. Selected catalysts active in FA decomposition.

Catalyst Precursor	Substrate	Solvent	T (°C)	Time (h)	TON	TOF (h ^{−1})
[RuCl ₂ (C ₆ H ₆) ₂]/DPPE [14]	HCO ₂ H	DMOA	25	1080	>1,000,000	1000
[(PNP ³)Ru(H)Cl(CO)] [10]	HCO ₂ H/NHex ₃	DMF	90	3	706,500	256,000
[Cp*Ir(pyrimidyl imidazoline)H ₂ O]SO ₄ [15]	HCO ₂ H/NaO ₂ CH	H ₂ O	100	0.17	68,000	322,000
[Cp*Ir(PHEN-diol)H ₂ O]SO ₄ [16]	HCO ₂ H	H ₂ O	60	2600	5,000,000	1900
[Cp*Ir(d)Cl]Cl, 3d (this work)	HCO ₂ H	H ₂ O	110	0.55	2150	3861

3.3. Catalytic Activity in the Hydrogenation of CO₂ Using the Complexes as Precatalysts

The direct hydrogenation of CO₂ was first studied using the **3c** complex (Scheme 4), which is one of the more stable and water-soluble complexes. The experiment was conducted from 80 to 140 °C (see Figure 6) to optimize the reaction temperature and achieve maximum conversion of triethylammonium formate, which was found to occur between 100 °C (0.89 ± 0.02 mmol) and 120 °C (0.93 ± 0.02 mmol). Therefore, the following experiments were performed at 110 °C.

**Scheme 4.** Catalytic hydrogenation of CO₂ to formate.

It was important to study the ratio of the mixture of gases, because in most previous reports, better conversions were observed using a CO₂:H₂ ratio of 1:1. The experiments were conducted with the **3c** complex, using a 1:1 or 1:2 CO₂:H₂ ratio (Figure 7). The maximum conversion of formate was achieved with a 1:2 CO₂:H₂ ratio (1.43 ± 0.02 mmol).

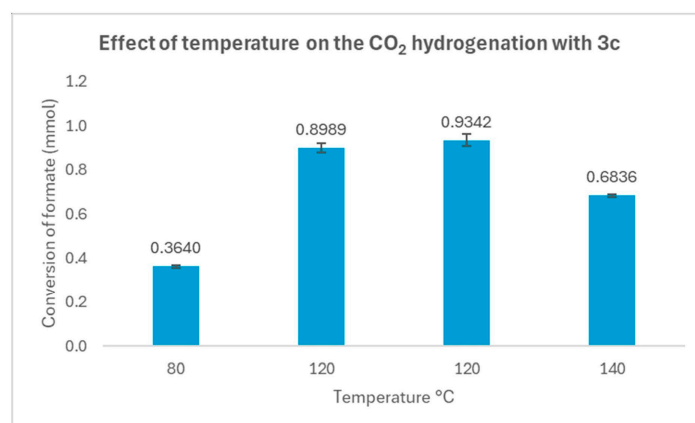


Figure 6. Effect of temperature on CO₂ hydrogenation, using **3c** as the precatalyst. Conditions: precatalyst (5 μ mol), H₂O (3 mL), NEt₃ (7.17 mmol), CO₂ (30 bar), H₂ (30 bar), temperature: 80 to 140 $^{\circ}$ C, and time: 20 h. The conversions of formate were determined via ¹H NMR spectroscopy, using DMF (132 μ L) as an internal standard.

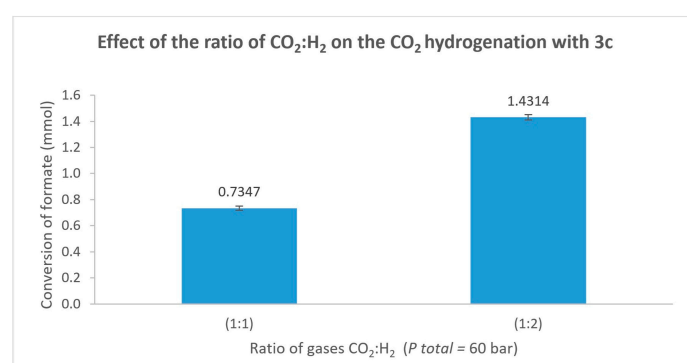


Figure 7. Effect of the ratio of CO₂:H₂ on CO₂ hydrogenation, using **3c** as a precatalyst. Conditions: precatalyst (5 μ mol), H₂O (3 mL), NEt₃ (7.17 mmol), *p*CO₂ + *p*H₂ (60 bar), temperature: 110 $^{\circ}$ C, and time: 20 h. The conversions of formate were determined via ¹H NMR spectroscopy, using DMF (132 μ L) as an internal standard.

In certain related studies, the effect of solvents in the catalytic reaction has been investigated [38]. Therefore, in this study, we investigated the direct hydrogenation of CO₂ using **3c** as a precatalyst in water and in a mixture of water and either ethanol or tetrahydrofuran (THF) in a ratio of 1:1 (Figure 8). The water/THF mixture produced the highest formate conversion (4.27 ± 0.04 mmol). We also evaluated various H₂O/THF ratios (2:1, 1:1, 1:2, and 1:5) (Figure 9), achieving the highest formate conversion with the 1:2 ratio (4.52 ± 0.02 mmol).

With all these optimizations, we studied the ruthenium (**1b–1e**), rhodium (**2a–2c**, **2e**), and iridium (**3a–3e**) complexes as precatalysts in the direct hydrogenation of carbon dioxide, in the presence of triethylamine, to yield triethylammonium formate (Scheme 4). The results are summarized in Table 5.

With these results, it is critical to note that the efficiency of ruthenium complexes in the direct hydrogenation of carbon dioxide to formate reached values of TON = 1474.5 (entry 12) and TOF = 69.2 (entry 15). The presence of the –OH protic group in complex **1c** (entries 12 and 13) indicates a better catalytic performance, while the high solubility of complex **1e** (entry 15) in THF could be the reason for the high conversion of formate. With respect to iridium complexes, they have a moderate efficiency (entries 2, 3, and 6) and their behavior matches previous observations, that is, the –OH protic groups in **3b** (entry 2) and **3c** (entry 3) and the solubility of **3e** in THF (entry 6) enhance catalytic

efficiency. The rhodium complexes presented a lower catalytic performance, and it is only worth highlighting the **2b** complex (entry 8), in which the –OH group exhibits the best performance compared to other rhodium complexes.

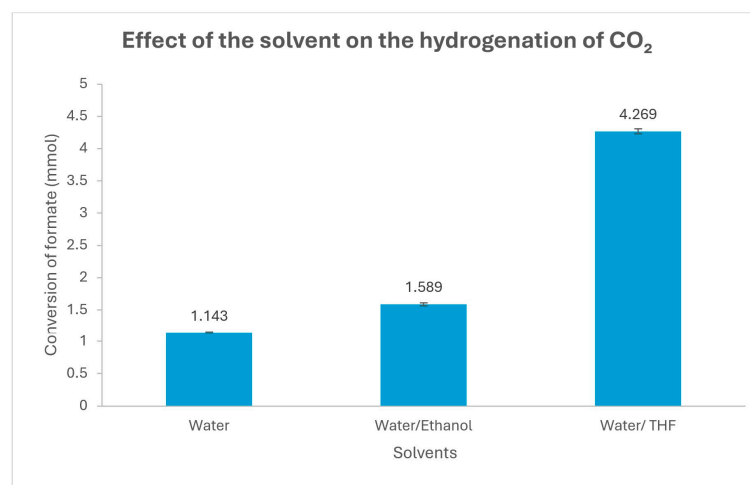


Figure 8. Effect of the solvent on CO₂ hydrogenation, using **3c** as a precatalyst. Conditions: precatalyst (5 μ mol), solvent: H₂O, H₂O/ethanol 1:1, H₂O/THF 1:1 (3 mL), NEt₃ (1 mL, 7.17 mmol), CO₂ (20 bar), H₂ (40 bar), temperature: 110 °C, and reaction time: 20 h. The conversions of formate were determined via ¹H NMR spectroscopy, using DMF (132 μ L) as an internal standard.

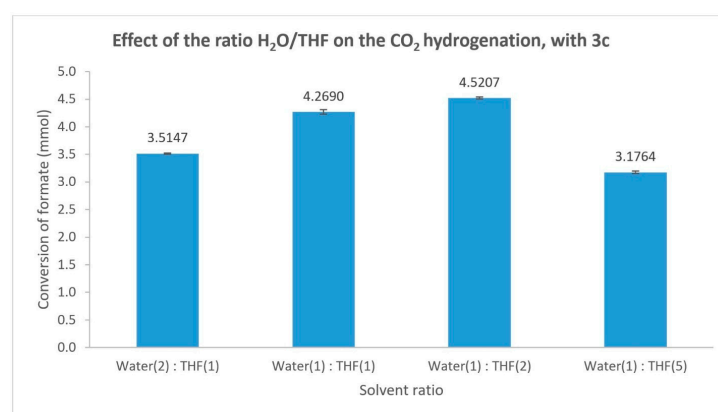


Figure 9. Effect of the H₂O/THF ratio on CO₂ hydrogenation, using **3c** as a precatalyst. Conditions: precatalyst (5 μ mol), solvent: H₂O/THF 2:1, 1:1, 1:2, 1:5 (3 mL), NEt₃ (1 mL, 7.17 mmol), CO₂ (20 bar), H₂ (40 bar), temperature: 110 °C, and time: 20 h. The conversions of formate were determined via ¹H NMR spectroscopy, using DMF (132 μ L) as an internal standard.

Table 5. Direct hydrogenation of CO₂ to formate using ruthenium, rhodium, and iridium complexes as precatalysts.

Entry	Complex	[HCOO [−]] (mmol)	Conversion (%)	TON	TOF (h ^{−1})
1 ^a	3a	0.94 ± 0.18	13.1	188.1	9.4
2	3b	4.74 ± 0.17	66.1	947.5	19.7
3	3c	4.53 ± 0.10	63.1	905.5	45.3
4 ^{a,b}	3c	2.53 ± 0.04	49.2	706.1	35.3
5	3d	1.00 ± 0.03	14.0	200.6	10.0
6	3e	4.22 ± 0.12	58.8	843.2	42.2
7	2a	1.37 ± 0.06	19.1	274.3	13.7
8	2b	2.33 ± 0.12	32.5	465.8	23.3
9	2c	1.25 ± 0.16	17.5	250.5	12.5

Table 5. Cont.

Entry	Complex	[HCOO [−]] (mmol)	Conversion (%)	TON	TOF (h ^{−1})
10	2e	0.89 ± 0.11	12.4	177.9	8.9
11	1b	5.47 ± 0.05	76.3	1094.8	54.7
12 ^c	1c	7.37 ± 0.10	100.0	1474.5	30.7
13	1c	6.19 ± 0.07	86.3	1237.6	61.9
14	1d	4.41 ± 0.38	61.6	882.9	44.1
15	1e	6.92 ± 0.05	96.6	1384.9	69.2

Conditions: Complex = precatalyst (5 μmol), solvent: H₂O/THF 1:2 (3 mL), NEt₃ (1 mL, 7.17 mmol), CO₂ (20 bar), H₂ (40 bar), temperature: 110 °C, and time: 20 h. The conversions of formate (mmol) were determined via ¹H NMR spectroscopy, using DMF (132 μL) as an internal standard. TON = (mmol of formate/mmol of precatalyst). TOF = TON/reaction time (h). ^a Measured in H₂O, CO₂ (30 bar), H₂ (30 bar). ^b With a drop of Hg. ^c Measured at 48 h.

To verify that the hydrogenation of carbon dioxide is also carried out in a homogeneous phase by the complexes and to exclude the action of nanoparticles, an experiment was conducted with a drop of mercury (Table 4, entry 4) added to complex **3c**, resulting in a slight decrease in conversion.

As in the previous catalytic reaction, the cyclic stability of the catalyst was studied by an experiment under the same established conditions. The **1e** complex showed competitive conversion over four cycles (Figure 10).

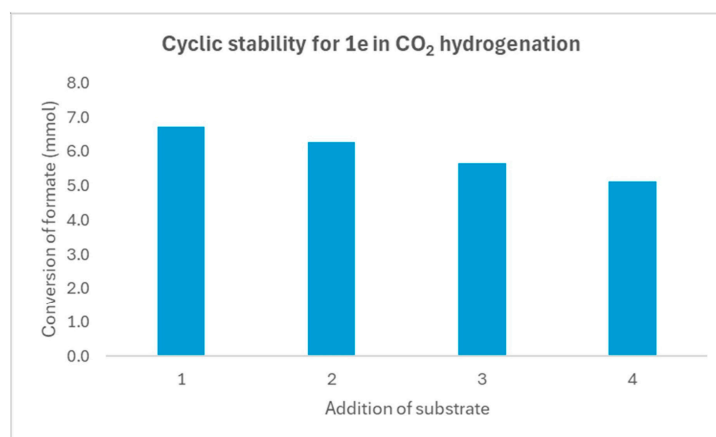


Figure 10. Cyclic stability in CO₂ hydrogenation, using **1e** as a precatalyst. Conditions: precatalyst (5 μmol), solvent: H₂O/THF 1:2, (3 mL), NEt₃ (1 mL, 7.17 mmol), CO₂ (20 bar), H₂ (40 bar), temperature: 110 °C, and time: 20 h. The conversions of formate were determined by ¹H NMR spectroscopy, using DMF (3.5 μL) as an internal standard.

Apparently, in CO₂ hydrogenation, the presence of protic groups –OH and –NH– does not increase efficiency as much as the solubility of the **1e** precatalyst and that of the CO₂ substrate in water/THF. Complex **1e** can be compared with other catalyst precursors reported in the literature for this reaction (Table 6).

Table 6. Selected catalytic systems that are active in hydrogenation of CO₂.

Catalyst Precursor	Solvent	Additive	P(CO ₂ /H ₂) (bar/bar)	T (°C)	Time (h)	TON	TOF (h ^{−1})
[(PNP ³)Ru(H)Cl(CO)] [10]	DMF	DBU	10/30	120	0.1	200,000	1,100,000
[(η ⁶ - <i>p</i> -cym)Ru(bis-NHC ¹)Cl]PF ₆ [11]	H ₂ O	KOH	20/20	200	75	23,000	300
[(PNP ¹)IrH ₃] [12]	H ₂ O/THF	KOH	30/30	120	48	3,500,000	73,000
[Ir(bis-NHC ²)(AcO)I ₂] [13]	H ₂ O	KOH	30/30	200	75	190,000	2500
[(η ⁶ - <i>p</i> -cym)Ru(e)Cl]Cl, 1e (this work)	H ₂ O/THF	NEt ₃	20/40	110	20	1385	69

4. Conclusions

Thirteen ruthenium(II), rhodium(III), and iridium(III) complexes bearing α -diimine ligands with $-\text{OH}$ or $-\text{NH}-$ protic groups were synthesized and characterized using NMR spectroscopy and ESI-MS. The structures of complexes **1d**, **3a**, and **3c** were confirmed using single-crystal XRD. The highly air-stable and water-soluble ruthenium(II), rhodium(III), and iridium(III) complexes were employed as precatalysts in FA decomposition, with complex **3d** achieving TON and TOF values of up to 2150 and 3861 h^{-1} , respectively, within short reaction times. The presence of protic $-\text{NH}-$ groups may promote the catalytic process. In CO_2 hydrogenation, we obtained TON and TOF values of up to 1385 and 69.25 h^{-1} , respectively, for complex **1e**. In this case, the enhanced solubility of the precatalyst in THF may have contributed positively to its performance. It is noteworthy to highlight the high activity of ruthenium complexes in the hydrogenation of carbon dioxide, increasing their relevance as a sustainable catalyst.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry7060196/s1>, Figures S1–S38: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra; Figure S39: ^1H NMR measurement of formate in CO_2 hydrogenation; Figures S40–S58: ESI-MS histograms; Figures S59–S71: IR spectra; Figures S72–S75: DSC thermograms; Table S1. Crystal data and structure refinement for complexes **1d**, **3a** and **3c**.

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