Iridium catalysts featuring amine-containing ligands for the dehydrogenation of formic acid

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Dedicated to Prof. Ekkehardt Hahn on the occasion of his 65th birthday with our most sincere congratulations for his leadership and his many diverse and creative contributions to the field of Organometallic Chemistry, and best wishes.

Abstract

The use of protic ligands to generate metal-ligand bifunctional catalysts has proved an excellent strategy to enhance the catalytic activity in formic acid dehydrogenation. We present here synthetic routes for complexes of general formula [Ir(H)2(IPr)(PR3)(CH3CN)2]BF4 (1a-c), [Ir(8-AQ)(H)2(IPr)(PR3)]BF4 (2a-c and 3), and [Ir(IPr)(C-N)(8-AQ)H]BF4 (5a-c) (8-AQ= 8-aminoquinoline; IPr = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene; C-N = 1-phenylpyridine-1H, 1-phenylpirazol-1H or 2-(p-tolyl-1H)pyridine-1H). Complexes 2a-c, 3, 5a and c were evaluated as catalysts for the dehydrogenation of formic acid in water. The nature of the phosphane in complexes 2a-c and 3 affects drastically the catalytic activity, with more basic and less encumbered phosphanes bringing about better performances. DFT calculations suggest that the coordinated NH2 moiety of the 8-AQ ligand plays a crucial role throughout the catalytic cycle. Two key steps are the protonation of the hydride ligand directed by the NH2 moiety (H2 formation), and the hydride abstraction to regenerate the dihydride active species (CO2 formation). Complexes 5a and 5c do not improve the results obtained with 2a-c and 3, probably due to the fact that a preactivation step is required. This may be attributable to an isomerization step that places the NH2, initially trans to the hydride ligand, in cis position.
The activity in the dehydrogenation of formic acid by organometallic iridium catalysts featuring the 8-aminoquinoline ligand was evaluated, and theoretical calculations that shed light on the role of the amine moiety in the reaction mechanism were carried out.

Keywords

NHC, iridium, formic acid, dehydrogenation, catalysis, reaction mechanism.
I. Introduction

The design of organometallic complexes equipped with protic ligands is a widespread strategy to prepare metal-ligand bifunctional catalysts. The reaction mechanisms that these catalysts bring about play a fundamental role in the hydrogenation of polar bonds, such as ketones or imines, and in its reverse reaction, the dehydrogenation of alcohols or amines.\[^{1}\] Probably the most representative example is Noyori’s catalyst, where an amine ligand that is bound to the Ru center by the lone pair of the nitrogen atom stabilizes the transition state by means of a N-H···O hydrogen bond interaction. This eventually leads to the reduction of the substrate (ketone or aldehyde) by transfer of a hydride ligand to the carbonyl carbon.\[^{2}\]

In recent years, the use of formic acid as a hydrogen storage material has seen an increasing interest, and a great wealth of dehydrogenation catalysts have been reported.\[^{3}\] Bifunctional catalysts in particular bring about excellent activities that can be ascribed to the stabilization of transition states by hydrogen bond interactions.\[^{4}\] In particular, protic ligands are able to interact with formic acid (e. g. transition states A\[^{5}\] and B\[^{6}\] in Figure 1) or H\(_2\)O (often used as solvent or co-solvent; e. g. transition states C\[^{7}\] and D\[^{8}\] in Figure 1) via hydrogen bond interactions, thus giving rise to low energy pathways that commonly involve proton transfer reactions.

![Figure 1. Examples of ligand assisted transition states proposed in the literature.](image-url)

The most active catalysts hitherto reported, either in neat formic acid or in aqueous solution, usually present an iridium atom as metal center; namely, [Ir(COD)(Bu\(_3\)PCH\(_2\)(2-py))]CF\(_3\)SO\(_3\)\[^{9}\] (TOF = 13320 h\(^{-1}\)) and [IrClCp*(2,2’-bi-2-imidazoline)]Cl\[^{10}\] (TOF = 487500 h\(^{-1}\)), respectively (COD = 1,5-cyclooctadiene; Cp* = pentamethylcyclopentadienyl). Remarkably, the excellent activity of the latter in water has been ascribed to the presence of a protic ligand. Other catalyst based on protic ligands that show excellent activities in pure water are the binuclear Ir catalyst described by Fujita and Himeda (TOF = 228000 h\(^{-1}\)),\[^{11}\] the Ir complex [IrCp\(^\ast\)(H\(_2\)O)(DHBP)]\(^{2+}\) (DHBP =
4,4'-dihydroxy-2,2'-bipyridine)\[^{12}\] (TOF = 14000 h\(^{-1}\)), and the Ru complex [Ru(p-cymene)(2,2'-bi-2-imidazoline)Cl]Cl\[^{13}\] (TOF = 12000 h\(^{-1}\)). Complexes of general formula [IrClCp*\(\delta\)(L)] (L = diphenylethylenediamine derivatives) give rise to TOF values of 4990\[^{8}\] and 11110 h\(^{-1}\)\[^{14}\] in water/1,2-dimethoxyethane mixtures.

In this regard, we have recently reported a new family of complexes that show good activities for the dehydrogenation of formic acid in water. The most active catalyst of the series, and the only one that can be recycled without an apparent loss of activity, is complex [Ir(H)\(_2\)\(\delta\)(8-AQ)(IPr)(PPhMe\(_2\))]BF\(_4\) (8-AQ= 8-aminoquinoline, IPr = 1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidene), which, in contrast with the other complexes tested in this work, features a protic ligand (8-AQ).\[^{15}\] The reaction mechanism is most likely related to that reported by Kayaki et al. (D), according to which the NH\(_2\) moiety of the 8-AQ ligand locks a molecule of water in the right position to promote protonation of the hydride ligand. Plausibly, this would generate a molecule of H\(_2\) and a vacant site where the formate could coordinate.

In this work, we evaluate how the modification of the phosphane ligand affects the activity of complexes of general formula [Ir(8-AQ)(H)\(_2\)(IPr)(PR\(_3\))]BF\(_4\). Moreover, the influence of the 8-aminoquinoline ligand in the catalytic activity of a new type of Ir-IPr complexes, namely [Ir(IPr)(C-N)(8-AQ)H]BF\(_4\), where C-N is 1-phenylpiridine-1H, 1-phenylpirazol-1H or 2-(p-tolyl-1H)pyridine-1H, was compared against their parent complexes [Ir(IPr)(C-N)(py)\(_2\)]BF\(_4\). Based on DFT calculations, we also propose a feasible reaction mechanism in agreement with experimental observations.

2. Material and methods

All experiments were carried out under an inert atmosphere using standard Schlenk techniques. The solvents were dried by known procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). Formic acid and water were degassed prior to use. The starting complexes [Ir(H)\(_2\)(IPr)(py)\(_3\)]BF\(_4\) was prepared according to the literature procedures.\[^{16}\] All other commercially available starting materials were purchased from Sigma-Aldrich, Merck and J. T. Baker and were used without further purification. H\(_2\) gas (>99.5%) was obtained from Infra. \(^1H, ^{13}C\{^1H\},^{31}P\{^1H\}\) and \(^19\)F spectra were recorded either on a Bruker Avance II 300 MHz or a Bruker Avance III 300 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (\(^1H, ^{13}C\{^1H\}\)). Coupling constants, J, are given in Hz. Spectral assignments were achieved by combination of \(^1H\)–\(^1H\) COSY, \(^13\)C APT, and \(^1H\)–\(^19\)C HSQC/CE/CE/CE experiments. GC-MS spectra were recorded on a Hewlett-Packard GC-MS system.

\[\text{Ir(H)}_{2}\{(CH_3CN)_{2}\}(IPr)(PPh_2Me)]BF_4 (1a)\]

A solution of [Ir(H)\(_2\)(IPr)(CH\(_3\)CN)\(_3\)]BF\(_4\) (60 mg, 0.08 mmol) in dichloromethane (5 mL) was reacted with PPh\(_2\)CH\(_3\) (14 \(\mu\)L, 0.08 mmol) and stirred for 2 h at room temperature. The resulting solution was evaporated and washed with diethyl ether to afford 1a as a white solid in 65% yield (50 mg, 0.052 mmol). \(^1H\) NMR (300 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.54 (t, \(J_{H,H} = 7.80, 2H, \text{H}_{P,IPr}\)), 7.39 – 7.19 (m, 14H, \(H_{\text{Ir},IPr} + \text{H}_{P,IPr}\)), 7.18 (d, \(J_{H,P} = 0.8, 2H, =CHN\)), 7.25 (hept, \(J_{H,H} = 6.9, 4H, CHCH_3\{IPr\}\)), 1.86 (d, \(J_{H,P} = 8.8, 3H, \text{PMe}\)), 1.70 (d, \(J_{H,P} = 1.0, 6H, CH_3\{CN\}\), 1.27 and 1.20 (both d, \(J_{H,H} = 6.9, 12H, CHCH_3\{IPr\}\)), \(-21.64\) (d, \(J_{H,P} = 17.7\) Hz, 2H, Ir-H). \(^{13}C\{^1H\}\)-APT NMR plus HSQC and HMBC (75 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 168.2
A solution of [Ir(H)(IPr)(CH_3CN)]_2BF_4 (100 mg, 0.13 mmol) in dichloromethane (5 mL) was reacted with PPh_3 (37 mg, 0.11 mmol) and stirred for 2 h at room temperature. The resulting solution was evaporated and washed with pentane to afford 1b as a white solid in 58% yield (75 mg, 0.075 mmol). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.53 (t, J_H-H = 7.79, 2H, H_p-IPr), 7.38 – 7.22 (m, 13H, H_ar-IPr + H_PPh), 7.18 – 7.07 (m, 8H, H_PPh + =CHN), 2.70 (hept, J_H-H = 6.9, 4H, CHCl_3-IPr), 1.48 (d, J_H-P = 0.9, 6H, CH_3CN), 1.19 and 1.16 (both d, J_H-H = 7, 12H, CHCl_3-IPr), −21.39 (d, J_H-P = 16.9, 2H, Ir-H). ^13C {^1H}-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2) δ 167.2 (d, J_C-P = 114, Ir-CP, 146.6 (s, C_3-IPr), 138.2 (s, NCIPr), 134.2 (d, J_C-P = 11, CHPPh), 133.3 (d, J_C-P = 50.5, C_4-IPr), 130.6 (s, CH_PIPr), 130.4 (d, J_C-P = 2.1, CH-PPh), 128.57 (d, J_C-P = 9.9, CH_PPh), 124.6 (d, J_C-P = 3.7, =CH), 124.3 (s, CH_3CN), 113.8 (s, CHCH_3-IPr), 25.6 and 22.6 (both s, CHCH_3-IPr), 3.1 (s, CH_3CN). ^31P NMR (121 MHz, CD_2Cl_2) δ −4.36 (s). ^19F NMR (282 MHz, CD_2Cl_2) δ −153.07 (s). HRMS (ESI) m/z calcd. for C_{44}H_{57}IrN_4PBF_4 (M-BF_4 -2CH_3CN) 783.3414 found 781.3491.

[Ir(H)(CH_3CN)(IPr)(PPh_3)]BF_4 (Ib)

A solution of [Ir(H)(IPr)(CH_3CN)]_2BF_4 (70 mg, 0.07 mmol) in dichloromethane (5 mL) was reacted with P(Pr)_3 (14 µl, 0.07 mmol) and stirred for 2 h at room temperature. The resulting solution was evaporated and washed with pentane to afford 1c as a white solid in 97% yield (62 mg, 0.068 mmol). ^1H NMR (300 MHz, CD_2Cl_2) δ 7.47 (t, J_H-H = 7.98, 2H, H_p-IPr), 7.31 (d, J_H-H = 7.98, 4H, H_m-IPr), 7.08 (m, J_H-P = 0.8, 2H, =CHN), 2.71 (hept, J_H-H = 6.9, 4H, CHCl_3-IPr), 2.00 (s, 6H, CH_3CN), 1.94–1.80 (m, 3H, CH_PIPr), 1.29 and 1.16 (both d, J_H-H = 6.9, 12H, CHCl_3-IPr), 0.90 and 0.86 (both d, J_H-H = 7.1, 18H, CH_3-IPr), −22.22 (d, J_H-P = 16.8, 2H, Ir-H). ^13C {^1H}-APT NMR plus HSQC and HMBC (75 MHz, CD_2Cl_2) δ 167.3 (s, Ir-CP), 146.6 (s, C_3-IPr), 138.4 (s, NCIPr), 130.6 (s, CH_PIPr), 124.6 (d, J_C-P = 3.5, =CHN), 124.3 (s, CH_m-IPr), 119.4 (s, CH_3CN), 29.2 (s, CHCH_3-IPr), 25.7 (s, CHCH_3-IPr), 24.9 (d, J_C-P = 26.6, CH_PIPr), 22.8 (s, CHCH_3-IPr), 19.6 (s, CH_3-IPr), 4.0 (s, CH_3CN). ^31P NMR (121 MHz, CD_2Cl_2) δ 24.16 (s). ^19F NMR (282 MHz, CD_2Cl_2) δ −153.14 (s). HRMS (ESI) m/z calcd. for C_{40}H_{60}IrN_4PBF_4 (M-BF_4 -2CH_3CN) 845.3575 found 845.3697.

[Ir(H)(CH_3CN)(IPr)(Pr(Pr)]_2BF_4 (Ic)

A solution of [Ir(H)(IPr)(CH_3CN)]_2BF_4 (30 mg, 0.03 mmol) in dichloromethane (2 mL) was reacted with 2 equivalents of 8-aminquinoline (5 mg, 0.04 mmol) and stirred for 2 h at room temperature. The resulting solution was evaporated and washed with pentane to afford 2a as a light brown solid in 55% yield (18 mg, 0.016 mmol). ^1H NMR (300 MHz, CD_2Cl_2) δ 8.05 (d, J_H-H = 8.3, 1H, H_AQ), 7.73 (d, J_H-H = 4.7, 1H, H_AQ), 7.66–7.53 (m, 3H, H_ar-IPr + H_PPh), 7.40 – 7.15 (m, 9H, H_ar-IPr + H_AQ + =CHN), 7.09 – 6.89 (m, 8H, H_PPh + H_AQ), 6.75-
A solution of 1a (42 mg, 0.04 mmol) in dichloromethane (2 mL) was reacted with 1.2 equivalents of 8- aminoquinoline (7 mg, 0.05 mmol) and stirred for 18 h at room temperature. The resulting solution was evaporated and washed with pentane to afford 2b as a light brown solid in 56% yield (25 mg, 0.022 mmol). 1H NMR (300 MHz, CD2Cl2) δ 7.89 (d, J=7.8 Hz, 3H, CHC=), 7.67–7.53 (m, 3H, Har=AO), 7.40 – 7.24 (m, 6H, Har=AO + Har=AO + HPh), 7.23 – 7.13 (m, 5H, HPh + =CHN), 7.08–6.96 (m, 7H, HPh), 6.97 – 6.84 (m, 6H, HPh + Har=AO), 6.58 (d, J=10.2 Hz, 1H, Har=AO), 4.30 and 3.77 (both d, J=2.1 Hz, 1H, Har=AO), 2.97–2.57 (m, 4H, CHCH3=), 1.17–1.07 (m, 12H, CHCH3=), 0.99 and 0.82 (both d, J=6.5 Hz, 6H, CHCH3=), –20.92 (dd, J=17.5 Hz, J=6.9 Hz, 6H, CHCH3=), –22.27 (dd, J=17.1 Hz, J=7.6 Hz, 1H, Har=AO), 13C {1H}-APT NMR plus HSQC and HMBC (75 MHz, CD2Cl2) δ 168.0 (d, J=11.4 Hz, 1H, Har=AO), 156.51 (s, CH2=), 147.3 (s, Cq=), 147.1 (s, Cq=), 146.6 (s, Cq=), 140.70 (s, Cq=), 137.3 (s, NC=), 135.7 (s, CH2=), 133.3 (d, J=10.9 Hz, HPh), 132.7, 132.6, 132.5 (d, J=49.5 Hz, C1), 131.1 (s, CH2=), 130.7 (s, Cq=), 130.3 (d, J=2.1 Hz, CHPh), 130.0 (s, CH2=), 128.7 (d, J=9.7 Hz, CHPh), 128.6 (s, CH2=), 127.9 (s, CH2=), 125.1 and 124.9 (both s, CH2=), 124.8 (s, =CHN), 124.0 (s, CH2=), 29.6 and 29.5 (both s, CHCH3=), 26.5, 26.1, 22.2 and 21.9 (all s, CHCH3=). 31P NMR (121 MHz, CD2Cl2) δ −22.52 (bs). 19F NMR (282 MHz, CD2Cl2) δ −153.27 (s). HRMS (ESI) m/z calcd for C49H30IrN4PBF4 (M-BF4) 989.4235 found 989.4235.
A solution of [Ir(H)(IPr)(CH$_3$CN)$_2$]BF$_4$ (40 mg, 0.05 mmol) in acetonitrile (5 mL) was reacted with sodium triphenylphosphine-m-sulfonate (TPPMS) (20 mg, 0.055 mmol) and stirred for 1 h at room temperature. The resulting solution was evaporated and redissolved in dichloromethane (5 mL). 8-aminoquinoline (14 mg, 0.1 mmol) was added and the mixture stirred for 5 h at room temperature. Then the solvent was evaporated and the residue was washed with diethyl ether and pentane to afford 3 as a light brown solid in 52% yield (28 mg, 0.026 mmol). $^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 7.87 (d, $J_{H-H}$ = 8.3, $J_{H-H}$ = 1.1, 1H, H$_{ar-AQ}$), 7.62–7.56 (m, 2H, H$_{ppn}$), 7.54–7.47 (m, 2H, H$_{ar-AQ}$ + H$_{ppn}$), 7.40–7.37 (m, 2H, H$_{ar-AQ}$), 7.34 – 7.19 (m, 10H, H$_{ppn}$ + H$_{ar-IPr}$), 7.18 – 7.06 (m, 5H, H$_{ppn}$ + =CHN), 7.03 – 6.95 (m, 2H, H$_{ppn}$ + H$_{ar-AQ}$), 6.93 – 6.86 (m, 1H, H$_{ppn}$), 6.82 – 6.75 (m, 1H, H$_{ppn}$), 6.66 (dd, $J_{H-H}$ = 8.4, 4.8, 1H, H$_{ar-AQ}$), 6.58 – 6.51 (m, 1H, H$_{ppn}$), 4.24 and 4.13 (both d, $J_{H-H}$ = 12.9, 1H, NH$_{2-AQ}$), 2.75 – 2.64 (m, 4H, CH$_2$CH$_3$-IPr), 1.14 – 1.08 (m, 12H, CH$_2$CH$_3$-IPr), 0.97 and 0.87 (both d, $J_{H-H}$ = 6.9, 6H, CHCH$_3$-IPr), 0.299 (dd, $J_{H-H}$ = 18.1, 1H, H$_{ar-H}$), 17.4 ($J_{H-H}$ = 7.6, 1H, Ir-H). $^{13}$C ($^1$H)-APT NMR plus HSQC and HMBC (75 MHz, CD$_2$Cl$_2$) $\delta$ 168.8 (s, Ir-CH$_3$), 156.3 (s, CH$_3$-AQ), 147.3 (s, C=Ar), 147.0 (s, C$_7$-AQ), 146.6 (s, C$_3$-IPr), 140.2 (s, C$_5$-AQ), 137.4 (s, NC$_3$-IPr), 135.9 (s, CH$_2$-AQ), 134.5 (d, $J_{C-P}$ = 11.3, C$_1$-PH$_2$), 133.9 (d, $J_{C-P}$ = 52.2, C$_5$-PPn), 133.5 (d, $J_{C-P}$ = 11.1, CH$_2$-PPn), 133.1 (s, C$_5$-P$_{3+3}$SO$_3$), 132.5 (d, $J_{C-P}$ = 11.3, CH$_2$-PPn), 131.3 (d, $J_{C-P}$ = 45.2, C$_5$-PP$_3$), 131.1 (s, CH$_2$-AQ), 130.6 (d, $J_{C-P}$ = 2.1, CH$_2$-PPn), 129.5 (d, $J_{C-P}$ = 10.8, CH$_2$-PPn), 128.7 (d, $J_{C-P}$ = 9.8, CH$_2$-PPn), 128.4 (d, $J_{C-P}$ = 10.6, CH$_2$-PPn), 128.1 (s, CH$_2$-AQ), 128.0 (s, CH$_2$-AQ), 127.9 (s, CH$_2$-AQ), 125.1 and 124.9 (both s, CH$_2$-IPr), 124.8 (s, =CHN), 123.9 (s, CH$_2$-AQ), 29.6 and 29.5 (both s, CH$_2$CH$_3$-IPr), 26.5, 26.1, 22.2 and 22.0 (all s, CH$_2$CH$_3$-IPr). $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$) $\delta$ 21.60 (bs). HRMS (ESI) m/z calcd. for C$_{54}$H$_{61}$IrN$_4$P$_4$F$_{14}$(M-BF$_4$) 887.4730 found 887.4770.

**Synthesis of [Ir(H)(Phpy-1H)(8-AQ)(IPr)]BF$_4$ (5a)**

[Ir(H)(Phpy-1H)(IPr)(py)$_2$]BF$_4$ (50 mg, 0.05 mmol) and 1.2 equivalents of 8-aminoquinoline (8.8 mg, 0.06 mmol) are dissolved in 5 mL of dichloromethane. The resulting yellow solution is stirred for 2 h at 50 °C. Subsequently, the solvent is evaporated under reduced pressure and the residue washed with diethyl ether (3 x 5 mL). Finally, the yellow solid thus obtained is dried in vacuo to afford the title product in 26% yield (12.7 mg, 0.013 mmol). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 8.67 (dd, $J_{H-H}$ = 4.9, 1.5, 1H, H$_{aq}$), 8.50 (dd, $J_{H-H}$ = 8.6, 1.5, 1H, H$_{aq}$), 7.90 (d, $J_{H-H}$ = 8.2, 1H, H$_{aq}$), 7.77 (d, $J_{H-H}$ = 8.2, 1H, H$_{pp}$), 7.58–7.40 (m, 8H, H$_{ar}$-IPr, H$_{aq}$, =CHN), 7.27 (dd, $J_{H-H}$ = 7.7, 1.6, 1H, H$_{ar}$-IPr), 7.18 (d, $J_{H-H}$ = 2.2, 1H, =CHN), 7.10 (d, $J_{H-H}$ = 7.5, 1H, CH$_2$-PPn), 7.04 – 6.95 (m, 3H, H$_n$), 6.64 (sept, $J_{H-H}$ = 4.1, 1H, H$_{ar}$-IPr), 6.52 – 6.44 (m, 1H, H$_{ar}$-IPr), 5.92 (d, $J_{H-H}$ = 5.8, 1H, H$_{ar}$-IPr), 3.77 (hept, $J_{H-H}$ = 6.8, 1H, H$_{IP}$), 3.54 – 3.38 (m, 1H, H$_{IP}$), 2.35 (hept, $J_{H-H}$ = 6.7, 1H, H$_{IP}$), 2.06 (hept, $J_{H-H}$ = 6.8 Hz, 1H, H$_{IP}$), 1.32 – 1.21 (m, 8H, CH$_2$CH$_3$-IPr), 1.08 (dd, $J_{H-H}$ = 6.8, 4.3, 7H, CHCH$_3$-IPr), 0.74 (t, $J_{H-H}$ = 6.2, 6H, CHCH$_3$-IPr), 0.37 (d, $J_{H-H}$ = 6.6, 3H, CHCH$_3$-IPr), –0.44 (d, $J_{H-H}$ = 6.7, 3H, CHCH$_3$-IPr), –22.02 (s, Ir-
H). $^{13}$C {$^1$H}-APT NMR plus HSQC and HMBC (75 MHz, CD$_2$Cl$_2$, 298 K): δ 167.4 (s, C$_q$-NPh$_r$), 158.4 (s, Ir-Cl$_{IPr}$), 157.3 (s, CH$_{ar}$-NPh$_r$), 148.0 (s, Ir-Cl$_{IPr}$), 147.8 (s, C$_q$), 146.9 (s, Ir-Cl$_{IPr}$), 146.7 (s, Ir-Cl$_{IPr}$), 145.8 (s, Ir-Cl$_{IPr}$), 145.2 (s, CH$_{ar}$-NPh$_r$), 144.2 (s, C$_q$), 139.5 (s, CH$_{IPr}$), 138.5 (s, NC$_q$-IPr), 137.7 (s, CH$_{ar}$-NPh$_r$), 137.7 (s, CH$_{IPr}$), 135.5 (s, NC$_q$-IPr), 131.4 (s, CH$_{ar}$), 130.9 (s, CH$_{ar}$), 130.0 (s, CH$_{ar}$), 128.8 (s, CH$_{ar}$), 128.4 (s, CH$_{ar}$-NPh$_r$), 126.4 (s, CH$_{IPr}$), 125.9 (s, CH$_{ar}$), 125.0 (s, CH$_{IPr}$), 124.8 (s, CH$_{ar}$), 124.7 (s, CH$_{IPr}$), 124.1 (s, CH$_{ar}$), 123.8 (s, CH$_{ar}$), 123.5 (s, CH$_{IPr}$), 121.5 (s, CH$_{ar}$-NPh$_r$), 121.2 (s, CH$_{ar}$), 118.9 (s, CH$_{ar}$-NPh$_r$), 28.9, 28.6, 28.4 and 28.3 (all s, CHCH$_3$-IPr), 27.3, 26.4, 25.7, 24.9, 23.4, 22.6, 20.4 and 19.2 (all s, CHCH$_3$-IPr). HRMS (ESI) m/z calculated for C$_{45}$H$_{53}$Ir$_5$N$_3$BF$_4$ (M-BF$_4$) 880.3928. Found 880.3922.

**Synthesis of [Ir(H)(p-tolpy-1H)(8-AQ)(IPr)]BF$_4$ (5e)**

[Ir(H)(p-tolpy-1H)(IPr)(py)$_2$BF$_4$] (40 mg, 0.04 mmol) and 1.2 equivalents of 8-aminoquinoline (7.1 mg, 0.05 mmol) are dissolved in 5 mL of dichloromethane. The resulting yellow solution is stirred for 2 days at 50 °C. Subsequently, the solvent is evaporated under reduced pressure and the residue washed with pentane (3 x 5 mL). Finally, the yellow solid thus obtained is dried in vacuo to afford the title product in 44 % yield (18.6 mg, 0.018 mmol). $^1$H RMN (300 MHz, CD$_2$Cl$_2$, 298 K): δ 8.75 (dd, J$_{H-H}$ = 4.7, 1.5, 1H, H$_{ar}$), 8.53 (dd, J$_{H-H}$ = 8.5, 1.5, 1H, H$_{ar}$), 7.93 (d, J$_{H-H}$ = 8.3, 1H, H$_{ar}$), 7.75 (d, J$_{H-H}$ = 8.4, 1H, H$_{ar}$), 7.63–7.47 (m, 7H, H$_{ar}$), 7.46–7.40 (m, 2H, H$_{ar}$), 7.31 (dd, J$_{H-H}$ = 7.6, 1.5, 1H, H$_{ar}$), 7.22 (d, J$_{H-H}$ = 2.1, 1H, H$_{ar}$), 7.14 (d, J$_{H-H}$ = 7.1, 1H, H$_{ar}$), 6.88 (dd, J$_{H-H}$ = 8.2, 1.4, 1H, H$_{ar}$-tolpy), 6.75 (s, 1H, H$_{ar}$-tolpy), 6.52–6.44 (m, 1H, H$_{ar}$), 5.96 (s, 1H, H$_{ar}$-tolpy), 3.78 (s, 1H, H$_{IPr}$), 3.48 (s, 1H, H$_{IPr}$), 2.42 (s, 1H, H$_{IPr}$), 2.37 (s, 3H, CH$_3$-tolpy), 2.10 (s, 1H, H$_{IPr}$), 1.34 (d, J$_{H-H}$ = 6.9, 3H, CHCH$_3$-IPr), 1.28 (d, J$_{H-H}$ = 6.7, 3H, CHCH$_3$-IPr), 1.15 (d, J$_{H-H}$ = 7.3, 3H, CHCH$_3$-IPr), 1.10 (d, J$_{H-H}$ = 6.6, 3H, CHCH$_3$-IPr), 0.77 (d, J$_{H-H}$ = 6.7, 6H, CHCH$_3$-IPr), 0.42 (d, J$_{H-H}$ = 6.7, 3H, CHCH$_3$-IPr), −0.40 (d, J$_{H-H}$ = 6.7, 3H, CHCH$_3$-IPr), −22.05 (s, Ir-H). $^{13}$C $^1$H-APT RMN, HSQC and HMBC (75 MHz, CD$_2$Cl$_2$, 298 K): δ 167.4 (s, CH$_{ar}$), 158.3 (s, CH$_{ar}$), 157.3 (s, CH$_{ar}$), 148.0 (s, CH$_{ar}$), 147.8 (s, CH$_{ar}$), 147.8 (s, CH$_{ar}$), 147.0 (s, CH$_{ar}$), 146.7 (s, CH$_{ar}$), 146.7 (s, CH$_{ar}$), 145.7 (s, CH$_{ar}$), 145.5 (s, CH$_{ar}$), 141.5 (s, CH$_{ar}$), 140.8 (s, CH$_{ar}$), 139.4 (s, CH$_{ar}$), 138.2 (s, CH$_{ar}$), 137.6 (s, CH$_{ar}$), 137.6 (s, CH$_{ar}$), 135.6 (s, CH$_{ar}$), 131.3 (s, CH$_{ar}$), 130.9 (s, CH$_{ar}$), 128.8 (s, CH$_{ar}$), 128.3 (s, CH$_{ar}$), 126.4 (s, CH$_{ar}$), 28.8, 28.7 and 28.4 (all s, CHCH$_3$-IPr), 27.2, 26.4, 25.1 and 22.6 (all s, CHCH$_3$-IPr), 21.6 (s, CH$_3$-tolpy), 20.5 and 19.2 (s, CHCH$_3$-IPr). $^{19}$F RMN (300 RMN, CD$_2$Cl$_2$, 298 K): δ −152.7 (s, BF$_4$). HRMS (ESI) m/z calculated for C$_{48}$H$_{55}$Ir$_5$N$_3$BF$_4$ (M-BF$_4$) 894.4084. Found 894.4066.

**General procedure for the Ir-catalyzed dehydrogenation of formic acid.**

The catalytic tests were carried out on a Man on the Moon series X102 kit (https://www.manonthemoontech.com/x102-gas-evolution.html), employing a reactor with a total volume of 19 mL. The standard procedure consist of the following steps: (i) under an argon atmosphere, the reactor was charged with a solution of sodium formate (1.5 mg, 0.025 mmol, 5 mol%) in 1 mL of water; (ii) the corresponding catalyst (0.0025 mmol, 0.5 mol%) was added as a solid to the solution; (iii) the reactor was closed and placed in a thermostated oil bath at 353K; (iv) once the pressure was stabilized, 20 μL (0.5 mmol) of formic acid was added with a syringe, upon which, the measurement was started. The gas formation was measured until the pressure value remained constant. The amount of gases (mmol) produced during the reaction was calculated using the Ideal Gas Law: PV = nRT.
Computational Methods

DFT calculations were carried out by means of the Gaussian09 software package, D.01 revision.\(^{[17]}\) In particular, we applied the B3LYP exchange-correlation functional,\(^{[18]}\) with the D3BJ dispersion correction scheme.\(^{[19]}\) We applied the def2-SVP basis for all the geometry optimizations, and further refined the energy results through single point calculations with the def2-TZVP basis set.\(^{[20]}\) We also used the “ultrafine” grid, as well as the PCM model (as implemented in the Gaussian09 package) for the solvent effects.\(^{[21]}\) The nature of the stationary points of the Potential Energy Surface was confirmed by means of analytical frequency analysis, as well as the calculation of the reaction pathways by following the intrinsic reaction coordinate for transition states. The Gibbs energies were corrected by removing the translational entropy contribution from dissolved species as reported by Morokuma and co-workers.\(^{[22]}\) The motivation for the choice of this methodology lies on its good performance for similar systems.\(^{[23]}\)

3. Results and Discussion

3.1. Synthesis and characterization of complexes 1a-c

Complexes of general formula \([\text{Ir}(\text{H})_2(\text{CH}_3\text{CN})_2(\text{IPr})(\text{PR}_3)]\text{BF}_4\) (1a-c) (IPr = 1,3-bis(2,6-disopropyl)imidazol-2-ylidene) were prepared from \([\text{Ir}(\text{H})_2(\text{CH}_3\text{CN})_2(\text{IPr})]\text{BF}_4\) in dichloromethane at room temperature and the corresponding phosphine, according to the reaction depicted in Scheme 1. The addition of 1 equivalent of phosphane results in the selective substitution of the acetonitrile ligand \textit{trans} to the IPr, which is probably highly labilized due to the strong \textit{trans} effect of NHC ligands.\(^{[24]}\) The \(^1\)H NMR spectra of complexes 1a-c show doublets at \(\delta -21.64\) (\(J_{\text{H-P}} =17.7\) Hz), -21.39 (\(J_{\text{H-P}} = 16.9\)) and - 22.22 (\(J_{\text{H-P}} = 16.8\)) ppm, respectively, which correspond to the two hydride ligands \textit{cis} to phosphane. The \(^{31}\)P NMR spectra presents singlet resonances at \(\delta -4.36\), 19.47, and \(\delta 24.16\) for 1a-c, respectively, which further supports the substitution of only one of the acetonitrile ligands. The cationic nature of the complex was confirmed by the \(^{19}\)F NMR spectra, which feature singlet resonances at \(\delta -153.07\) (1a), -153.18 (1b) and -153.14 (1c) ppm.

\[
\text{CH}_3\text{CN} \quad \text{CH}_3\text{CN} \quad \text{BF}_4
\]

Scheme 1. Synthesis of complexes 1a-c from \([\text{Ir}(\text{H})_2(\text{CH}_3\text{CN})_2(\text{IPr})(\text{PR}_3)]\text{BF}_4\).

3.2. Synthesis and characterization of complexes 2a-c and 3

Complexes 1a-c were employed as starting materials for the preparation of complexes 2a-c, of general formula \([\text{Ir}(\text{H})_2(8\text{-AQ})(\text{IPr})(\text{PR}_3)]\text{BF}_4\). Complexes 2a-c feature phosphanes of different nature in order to study their influence in the catalytic activity of this complexes in formic acid dehydrogenation, and also allowing direct comparison with the complex \([\text{Ir}(\text{H})_2(8\text{-AQ})(\text{IPr})(\text{PPhMe}_2)]\text{BF}_4\) previously reported by us.\(^{[15]}\)
The reaction of 1a-c with 8-AQ in dichloromethane at room temperature affords complexes 2a-c, where the 8-AQ replaces the acetonitrile ligands trans to the two hydrides in complexes 1a-c. Upon coordination of the 8-AQ ligand, the position trans to the hydride ligands is now occupied by the amino and pyridyl moieties of the 8-AQ; therefore, the two hydride ligands become inequivalent. Consequently, the doublet at high field that appears in the $^1$H NMR spectra of 1a-c becomes two doublets of doublets due to coupling with the cis hydride and phosphane ligands. The new resonances emerge at $\delta$ –21.48 ($J_{H-P} = 18.2$ and $J_{H-H} = 7.5$ Hz) for 2a, –20.92 ($J_{H-P} = 17.5$ and $J_{H-H} = 7.6$ Hz) for 2b, and –22.38 ($J_{H-P} = 19.5$ and $J_{H-H} = 8.1$ Hz) for 2c. The characteristic cis $J_{H-P}$ coupling constants discard the possibility of the phosphane occupying one of the positions trans to one of the hydrides. Besides, it is noteworthy that the protons of the NH$_2$ moiety of the 8-AQ are diastereotopic. This is due to the different environments above and below the plane defined by the two hydride ligands and the two N’s of the 8-AQ, which gives rise to two broad doublets according to an AX system for the NH$_2$ protons. The $^{31}$P NMR spectra of 2a-c feature singlet resonances at $\delta$ 0.38, 22.52 and 19.06 ppm, respectively, in agreement with the structure proposed in Scheme 2. Analogously to 1a-c, the $^{19}$F NMR spectra of 2a-c feature singlet resonances at $\delta$ –153.02 (2a), –153.27 (2b) and –153.04 (2c) ppm.

![Scheme 2. Synthesis of complexes 2a-c from 1a-c.](image)

Complexes 2a-c are only partially soluble in water, therefore, in order to improve their catalytic activity in the dehydrogenation of HCOOH in aqueous solution, we attempted the synthesis of a related water-soluble complex featuring a TPPMS ligand (TPPMS = PPh$_2$(m-C$_6$H$_4$SO$_3$Na)). Thus, complex 3 was prepared by reaction of [Ir(H)$_2$(CH$_3$CN)$_3$(IPr)]BF$_4$ with TPPMS followed by addition of 8-AQ to the phosphane complex formed in situ (Scheme 3). Complex 3 shows similar patterns to those described above for complexes 2a-c in the $^1$H and $^{31}$P NMR spectra. The $^1$H NMR spectrum shows two doublets of doublets at $\delta$ –20.99 ($J_{H-P} = 18.1$ and $J_{H-H} = 7.7$ Hz) and –22.21 ($J_{H-P} = 17.4$ and $J_{H-H} = 7.6$ Hz) ppm, while the $^{31}$P NMR presents a singlet $\delta$ 21.6 ppm. In contrast with complexes 2a-c, 3 shows no resonance in the $^{19}$F NMR spectrum, which supports the zwitterionic nature of the complex depicted in Scheme 3.
Scheme 3. Synthesis of complex 3 from [Ir(H)2(CH3CN)3(IPr)]BF4.

3.3. Catalytic activity of complexes 2a-c and 3 in the dehydrogenation of formic acid

The influence of the phosphane ligand in the dehydrogenation of HCOOH was evaluated by employing a variety of complexes of general formula [Ir(H)2(8-AQ)(IPr)(PR3)]BF4 (2a-c and 3) as catalysts. The progress of the reaction was monitored using a reactor equipped with a pressure transducer (Man on the Moon series X102 kit). The catalytic studies were performed in water under the reaction conditions previously reported by us for the dehydrogenation of HCOOH using [Ir(H)2(8-AQ)(IPr)(PMe2Ph)]BF4 as catalyst; namely, 0.5 mol % of catalyst and 5 mol % of HCOONa at 80 °C.\textsuperscript{[15]}

Complex 2c, which features a P(Pr)3 ligand, shows the best activity among complexes 2a-c and 3, reaching a 55% conversion after 180 minutes (Figure 2). However, the activity of 2c is far from that reported for [Ir(H)2(8-AQ)(IPr)(PPhMe2)]BF4, which achieves full conversion after 8 minutes under analogous reaction conditions. Complex 3, which contains a water-soluble phosphane (PPh2(m-C6H4SO3Na)), shows an improved catalytic activity compared to its structurally related complex 2b (PR3 = PPh3), giving a 30% and 7% conversion, respectively, after 180 minutes. Nevertheless, the presence of a triaromatic phosphane trans to the NHC gives rise to a significant drop of the catalytic performance. On the other hand, complex 2a (PR3 = PPh2Me) performs marginally better than 2b (PR3 = PPh3). These results suggest that small and basic phosphane ligands bring about better catalytic activities. Therefore, we attempted the synthesis of the related complex [Ir(H)2(8-AQ)(IPr)(PMe3)]BF4; however, an intractable mixture of complexes was obtained due to the fact that other species with more than one PMe3 ligand were obtained together with the desired product.

![Figure 2](image_url)

**Figure 2.** Reaction profiles for the Ir-catalyzed dehydrogenation of HCOOH in H2O. Reaction conditions: 0.5 mmol of HCOOH, 0.5 mol % Ir catalyst, and 5 mol % HCOONa, at 80 °C in 1 mL of H2O.

3.4. DFT calculations on the mechanism of formic acid catalyzed by [Ir(H)2(8-AQ)2(PR3)]BF4 complexes

Computational studies at the DFT level using the B3LYP-D3BJ functional were carried out in order to gain new insights on the mechanism of HCOOH dehydrogenation by
We considered complex \([\text{Ir(H)}_2(8-\text{AQ})(\text{IPr})(\text{PR}_3)]\text{BF}_4\) (A) as model for the catalyst, and the most reasonable pathways are depicted in Figure 3. Notice that, for the sake of clarity, structures are referred to by letters starting form A. According to our calculations, the first step involves the protonation of one of the hydride ligands, resulting in the concomitant formation of molecular hydrogen and the amido-aquo species B. The NH$_2$ moiety of the 8-aminoquinoline ligand directs the proton transfer according to TS$_{A-B}$, showing and energetic barrier of 23.0 kcal·mol$^{-1}$, which occurs via a bridge formed by two molecules of water that interact with the organometallic complex by hydrogen bond interactions. Notice that we also computed the transition structure with only one water molecule, but it was 10.0 kcal·mol$^{-1}$ higher in energy. At this stage, B may react with a molecule of HCOOH to give E, or with formate to give C, releasing a molecule of H$_2$O. The latter is the lowest energy pathway, and, therefore, the most likely mechanism. Subsequently, the amido ligand in C is protonated by a molecule of formic acid to give D via TS$_{C-D}$. Finally, the coordination of a new molecule of formic acid aids the dissociation of the formate ligand and the subsequent hydride abstraction step by means of hydrogen bond interactions, which regenerates A with concomitant release of CO$_2$ and the HCOOH molecule via TS$_{D-A}$. It is noteworthy that the decoordination of the formate is mandatory since the formation of CO$_2$ cannot take place by β-hydride elimination due to the lack of vacant coordination sites (see SI); therefore, a hydride abstraction reaction must operate here.$^{[26]}$ According to the energy spam model proposed by Kzuch et al.$^{[27]}$ the overall activation energy of the process would be 23.0 kcal·mol$^{-1}$, and corresponds to the water-assisted hydride protonation process.

An alternative mechanism can be proposed from intermediate E, leading to two competitive pathways. The first, marked in red, would afford D by TS$_{E-D}$, which entails the protonation of the amido ligand by HCOOH followed by elimination of a molecule of formic acid, resulting in an activation barrier of 27.9 kcal·mol$^{-1}$. The second, marked in grey, would proceed from E via intermolecular protonation of the hydride ligand by the coordinated HCOOH (TS$_{E-F}$) to furnish F with concomitant liberation of H$_2$. Finally, analogously to TS$_{D-A}$, the release of CO$_2$ takes places by means of a hydride abstraction assisted by a molecule of HCOOH via a previous rearrangement of F that situates the C-H bond of the coordinated formic acid in the proximity of the formate’s oxygen. In this case, the overall activation energy of the process would be 36.7 kcal·mol$^{-1}$. Notice that the energy barriers involved in the last two pathways (27.9 kcal·mol$^{-1}$ for the “grey” and 36.7 kcal·mol$^{-1}$ for the “red” pathway in Figure 3) are much higher than those reported for the “blue” one, which features an effective energy barrier of 23.0 kcal·mol$^{-1}$. As a result, the “blue” pathway is the most likely of the alternatives postulated here.
Figure 3. DFT calculated Gibbs free energy profile (in kcal·mol$^{-1}$ and relative to A) for the Ir-catalyzed dehydrogenation of HCOOH.
3.5. Synthesis and characterization of complexes 5a-5c

A new type of complexes, 5a-c, was prepared by reaction of 8-aminoquinoline with the cyclometalated complexes [Ir(H)(Phpy-1H)(py)2(IPr)]BF4 (4a), [Ir(H)(PhPz-1H)(py)2(IPr)]BF4 (4b) and [Ir(H)(p-tolpy-1H)(IPr)(py)2]BF4 (4c) (where, Phpy = 2-phenylpyridine-1H, PhPz = 2-phenylpyrazole-1H and p-tolpy-1H = 1-tolylpyridine-1H), previously reported by us. The reaction was performed in CH2Cl2 at 50 ºC. 5a ([Ir(H)(Phpy-1H)(8-AQ)(IPr)]BF4) was obtained quantitatively after 2 h, while 5c ([Ir(H)(PhPz-1H)(8-AQ)(IPr)]BF4) required 2 days to reach full conversion. In the case of 5b ([Ir(H)(p-tolpy-1H)(8-AQ)(IPr)]BF4), the reaction rendered an intractable mixture of complexes, which prevented its isolation and characterization. However, crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of the crude reaction mixture in CH2Cl2. The reaction was monitored by 1H MNR spectroscopy. The spectra of 4a and 4c show singlet resonances at δ −18.13 and −18.09 ppm, respectively, for the hydride ligand that shift to δ −22.02 and −22.05 ppm, respectively, upon formation of 5a and 5c. In addition, in contrast with complexes 4a and 4c, the doublet that corresponds to IPr’s methyl groups of 5a and 5c shift to unusually high fields (from δ 0.40 ppm in 4a and 0.34 ppm in 4b to δ −0.44 ppm in 5a and −0.40 ppm in 5c). This atypical chemical shifts may be attributed to the anisotropic shielding generated by the ring current of the 8-AQ ligand, which are disposed orthogonally relative to the methyl groups pointing toward the metal center.

![Scheme 5. Synthesis of complexes 5a-c from 4a-c.](image)

To our surprise, the crystal structures of complexes 5b and 5c reveal that the coordination of 8-AQ results in the reorganization of the ligand system. In complexes 5a-c the N-donor group of the cyclometalated ligand is trans to the NHC, which contrasts with complexes 4a-c, where it is trans to the hydride. The other two coordination sites are occupied by the 8-AQ ligand, with the NH2 moiety trans to the hydride (Figure 4).
Figure 4. ORTEP view of 5b and 5c (ellipsoids are drawn at the 50% probability level). Counterions, solvent molecules and most hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): 5b: Ir-C(1) 2.003(3), Ir-C(41) 2.036(3), N(30)-Ir 2.113(3), N(40)-Ir 2.242(3), Ir-N(48) 2.078(3), C(1)-Ir-N(30) 98.89(12), C(1)-Ir-N(48) 170.98(12), N(30)-Ir-N(40) 78.27(11), C(41)-Ir-N(48) 79.37(13), C(1)-Ir-C(41) 91.73(14), C(1)-Ir-N(40) 102.28(14). 5c: C(1)-Ir 2.006(4), C(41)-Ir 2.022(4), N(30)-Ir 2.131(3), N(40)-Ir 2.227(3), N(48)-Ir 2.108(3), C(1)-Ir-N(30) 98.80(12), C(1)-Ir-N(48) 171.29(13), N(30)-Ir-N(40) 78.37(12), C(41)-Ir-N(48) 79.73(13), C(1)-Ir-C(41) 91.95(14), C(1)-Ir-N(40) 101.88(13).

The Ir center in 5b and 5c is in a distorted octahedral environment, plausibly due to steric constrains resulting from the proximity of the diisopropylphenyl rings of the NHC and the 8-AQ ligand. This brings about wide C(1)–Ir–N(30) and C(1)–Ir–N(40) angles, namely, 98.89(12)° and 102.28(14)° for 5b, and 98.80(12)° and 101.88(13)° for 5c, respectively. The steric tension also gives rise to a marked deviation from the ideal coordination of the NHC ligand to the metal center. Indeed yaw angles of 1.5° for 5b and 1.7° for 5c were observed along with pitch angles of 12.8° for 5b and 11.2° for 5c.[28]

It is worth mentioning that 5a-c are chiral-at-metal complexes,[29] with the two possible configurations being those depicted in Figure 5, i.e. 5 and 5’. Due to the centrosymmetric space group of both 5b (C2/c) and 5c (P–1), the crystals of 5b and 5c contain both configurations in a 1:1 ratio. On this basis, it is reasonable to believe that a racemic mixture is obtained for complexes 5a as well.
A plausible reaction mechanism for the formation of complexes 5a-c is depicted in Scheme 6. This mechanism was substantiated by theoretical calculation at the DFT level using the B3LYP-D3BJ functional employing as model the formation of 5c from 4c. The first step of the mechanism entails: (i) the dissociation of the Phpy-H’s pyridine moiety in 4c, which is labilized by the strong trans effect of the hydride ligand, and (ii) concomitant dissociation of one pyridine ligand followed by coordination of the Phpy-H’s pyridine moiety trans to the NHC, thus leaving a vacant coordination site trans to the hydride ligand. The energetic cost of this step is 15.9 kcal·mol⁻¹. Subsequently, coordination of the 8-AQ’s pyridinic nitrogen takes place in the position trans to the Phpy-H’s phenyl group, which causes the py ligand to occupy the position trans to the hydride ligand. Finally, the 8-AQ’s NH₂ moiety substitutes the py ligand, occupying the position trans to the hydride. This last step is driven by the high trans effect of the hydride ligand, which labilizes the py ligand, and the chelate effect of 8-AQ ligand, which stabilizes 5c, being the overall process slightly endergonic, +1.8 kcal·mol⁻¹.

Scheme 6. Reaction mechanism proposed for the formation of complexes 5c from 4c (energies are given kcal·mol⁻¹).

3.6. Catalytic activity of complexes 5a and 5c in the dehydrogenation of formic acid

The catalytic activity of complexes 5a and 5c was evaluated under analogous conditions to those described above for complexes 2a-c and 3 (Figure 6). 5c showed full conversion after 150 min, thus leading to slightly better activities than 2a-c and 3, which barely reach a 50% conversion after 150 min, but still much lower than that obtained with [Ir(H)₂(8-AQ)(IPr)(PPhMe₂)]BF₄. On the other hand, 5a requires over 400 min to reach full conversion and 150 min to achieve a 50% conversion, thus showing a similar activity to 2c, the most active catalyst reported in this work. It is worth mentioning that, in the case of complexes 5a-c, the NH₂ moiety of the 8-AQ ligand is not cis to the hydride ligand. Therefore, either the precatalysts undergoes an isomerization process that situates the NH₂ cis to the hydride, thus generating the active species, or the use of 5a-c as catalyst prompt an alternative mechanism. In this regard, the reaction profile of catalyst 5c (Figure 6) shows a sigmoidal curve, which may be due to a preactivation step. Arguably, the activation of the catalyst could be the isomerization step that situates the NH₂ cis to the hydride ligand. In this regard, the higher steric constrains that arise from the presence of the methyl group of the p-tolpy-H ligand, which points toward the bulk IPr ligand in 5c, may ease the isomerization step. In fact, a release of steric hindrance can be expected upon an isomerization process that entails the rearrangement of the p-tolpy-H ligand to the equatorial plane. This hypothesis is supported by the fact that, in complexes 4a-c, the cyclometallated ligand is in the equatorial plane. It is noteworthy that this happens even though there are two available coordination sites, occupied the pyridine ligands, which could allow a conformation of the p-tolpy-H ligand analogous to that in 5c.
Figure 6. Reaction profiles for the Ir-catalyzed dehydrogenation of HCOOH in H₂O with complexes 5a and 5c. Reaction conditions: 0.5 mmol of HCOOH, 0.5 mol % Ir catalyst, and 5 mol % HCOONa, at 80 °C in 1 mL of H₂O.

Conclusions

We have prepared a series of complexes of general formula [Ir(H₂)(8-AQ)(IPr)(PR₃)]BF₄ that were successfully tested as catalysts for the dehydrogenation of formic acid. However, the use of PPh₂Me, PPh₃, PPr and PPh₂(m-C₆H₄SO₃Na) as phosphane ligand instead of PPhMe₂ leads to a significant drop of the catalytic activity. Plausibly, according to the results obtained here, small and strong σ-donor phosphanes give rise to more active catalysts. Based on theoretical calculations, we proposed a reaction mechanism for these catalysts where the coordinated NH₂ moiety of the 8-AQ ligand directs the protonation of the hydride (to expel H₂) by means of hydrogen bond interaction with the water molecules of the solvent. The resulting aquo complex coordinates a molecule of formate. Then, the amido ligand is then able to deprotonate a molecule of formic acid, thus regenerating the NH₂ moiety and the formate. Finally, a molecule of HCOOH assists the hydride abstraction step, thus affording a molecule of CO₂, and the regeneration of the dihydride active species.

We also described a new family of chiral-at-metal Ir-complexes ([Ir(H)(C-N)(8-AQ)(IPr)]BF₄) and tested their activity as formic acid hydrogenation catalysts. These catalysts do not improve the results obtained with [Ir(H₂)(8-AQ)(IPr)(PR₃)]BF₄ complexes, perhaps due to the need for an isomerization step that places the NH₂ cis to the hydride ligand as preactivation of the catalyst.

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References


