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Supplementary Information for

A Metal-organic Framework Supported Iridium Catalyst for the Gas Phase Hydrogenation of Ethylene

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SI 1.0 Experimental section

SI 1.1 General Experimental Considerations

Single crystals of MOF **1** were prepared as previously reported.¹ The chemicals ethylene, hydrogen, $[Ir(C_2H_4)_2Cl]_2$, [acetaldehyde] were purchased from commercial vendors and used as received. Samples were handled under standard Schlenk techniques unless otherwise stated. Solvents were dried using literature procedures and degassed with Ar prior to use. Specifically, EtOH was dried by refluxing over Mg under N₂; acetone was dried from CaSO₄ under nitrogen; and pentane was dried over Na/benzophenone. NaBF₄ and NaCl used for anion exchange were stored in a 120°C drying oven.

Powder X-ray diffraction (PXRD) data were collected on a Bruker Advanced D8 diffractometer (capillary stage) using Cu K α radiation (λ = 1.5456 Å, 40 kW/ 40mA, 2 θ = 2 – 52.94°, phi rotation = 20 rotation/min, at 1 sec exposure per step with 5001 steps and using 0.5 mm glass capillaries). Solution NMR spectra were recorded on Varian 500 or 600 MHz instruments at 23°C using a 5 mm probe. Gas phase NMR spectra were collected on a Varian Gemini 600MHz NMR spectrometer as described below. Infrared (IR) spectra were collected on a Perkin-Elmer Spectrum Two, with the sample distributed between two NaCl disks in Nujol. High-resolution transmission electron microscopy (HRTEM) images and diffraction pattern were acquired using an uncorrected FEI Titan Themis 80-200. Energy dispersive X-ray spectroscopy (EDX) was performed on a Philips XL30 field emission scanning electron microscope. Gas adsorption isotherm measurements were performed on an ASAP 2020 Surface Area and Pore Size Analyser. Activation of samples was carried out as described.

SI 1.2 Preparation of 1·IrCl

Single crystals of **1** (~24 mg) were placed in a 20ml glass pressure vessel fitted with a pressure gauge and Swagelok tap assembly.² The crystals were washed with freshly distilled ethanol (5 x 5 ml) under Ar flow a total of 5 times (the solution was degassed with Ar after each exchange and the sample was allowed to soak for 1hr between washings). The solution was degassed with ethylene, excess $[Ir(C_2H_4)_2Cl]_2$ (30 mg) was added and the pressure tube was sealed under ethylene (~1.2 bar) and heated at 40°C for 24 hr. The resulting yellow crystals were washed with freshly distilled, ethylene degassed ethanol (5 x 5 ml) to remove dissolved Ir precursor. Insoluble Ir by-products were removed by washing the MOF crystals with dry, ethylene degassed acetone (5 x 5 ml) under ethylene flow to give **1**·IrCl as yellow crystals. IR v_{max} (nujol, cm⁻¹): 2050, 2016, 1985, 1925, 1608, 1555, 1376, 1304, 1273, 1226, 1173, 1152, 1089, 1049.

SI 1.3 Preparation of 1·IrBF₄

Single crystals of **1**·IrCl (~24 mg) were placed in a 20 ml glass pressure vessel fitted pressure gauge and Swagelok tap assembly. The crystals were washed with freshly distilled methanol (5 x 5 ml) under ethylene flow a total of 5 times (the solution was degassed with ethylene after each exchange and the sample was soaked for 1 hr between washings). Excess oven dried NaBF₄ was added to a small glass ampule which was subsequently submerged in the glass pressure tube containing the **1**·IrCl crystals. The pressure tube was sealed and allowed to stand at RT for 7 days (BF₄). Under ethylene flow, the ampule containing undissolved salt was removed and the yellow MOF crystals were washed with freshly distilled, ethylene degassed methanol (5 ml) five times under ethylene flow. IR v_{max} (nujol, cm⁻¹): 2092, 2019, 1934, 1613, 1555, 1376, 1305, 1273, 1181, 1143, 1096, 1067, 1033, 1016.

SI 2.0 Energy Dispersive X-ray (EDX) Analysis

Table S1: EDX analysis data for the iridium and associated anion occupancy determined via

 measurement of the Mn:Ir and Ir:Cl ratios.

Sample	Ir occupancy (%) ^{a,b}	Cl occupancy (%) ^{a,b}	Std error (%)
1·lrCl	81.5	80.4	7.2
1·IrBF ₄	78.2	0.2	5.4

^{*a*} Average atomic% obtained from three areas.

^b Relative to full occupancy of the bis(pyrazole)methane coordinating sites in **1**.



Figure SI 2.1: Representative raw EDX spectra for $1 \cdot [Ir(C_2H_4)_2CI]$



Figure SI 2.2: SEM images of metalated **1** showing (left) a single crystal and (right) an area of crushed crystals used for EDX analysis.

SI 3.0 High Resolution Transmission Electron Microscopy (HR-TEM) data



Direct Mag: 9300 x Adelaide Microscopy

Figure SI 3.1: Characterisation of **1**·IrCl after ethylene hydrogenation experiments. a) HR-TEM image and b) locally amplified HR-TEM. The images showed no detectable iridium nanoparticles.



Figure SI 3.2: Characterisation of $1 \cdot IrBF_4$ after the ethylene hydrogenation experiments. a) HR-TEM image and b) locally amplified HR-TEM. The images showed no detectable iridium nanoparticles.

SI 4.0 Powder X-ray Diffraction (PXRD) data



Figure SI 4.1: Experimental PXRD plots for 1-IrCl before and after ethylene hydrogenation experiments.



Figure SI 4.2: Experimental PXRD plots for **1**·IrBF₄ before and after ethylene hydrogenation experiments.

SI 5.0 Single Crystal X-ray Crystallography

SI 5.1 General Procedures

Single crystals were mounted in Paratone-N oil on a MiTeGen micromount. Single-crystal X-ray data were collected at 100 K on the MX1 beamline of the Australian Synchrotron³ using the Blue-ice software interface,⁴ λ = 0.71073 Å. Absorption corrections were applied using empirical methods, the structure solved using SHELXT^{3,4} and refined by full-matrix least squares on F² by SHELXL,⁵ interfaced through the program X-Seed⁶ or OLEX.⁷ Figures were produced using the program CrystalMaker. X-ray experimental data is given in Table S2. CIF data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers CCDC 2025173.

SI 5.2 Specific Refinement Details for 1·IrCl

For most of the MOF structure the atoms were refined anisotropically and hydrogens atoms were included as invariants at geometrically estimated positions. However, for the bridging ligand (the site of postsynthetic metalation), which is disordered over two positions, the less occupied component (A, 0.25 occupancy) and its associated Ir centre (Ir3A) were refined with isotropic refinement parameters. For the main component of the bridging ligand (B, 0.75 occupancy), anisotropic displacement parameters were used in the refinement. The disordered Ir centres are both on the mirror plane and combined refined to an approximately 0.3 occupancy (0.05 vs 0.25 occupancy for Ir3A vs Ir3B); this is slightly lower than the metalation yield measured by Energy Dispersive X-ray analysis of ca. 80%, i.e. 0.4 occupancy. The coordinated ethylene, which was fixed at 0.25 occupancy in line with the refined occupancy for Ir3B, was also refined with isotropic displacement parameters. The low occupancy of the Ir3A site and the disorder of the overall metalation site precluded identification of the coordination environment, but a partial CO and ethylene ligand was included in the formula in line with the data provided by IR spectroscopy. Overall this model represents the structure as a [Ir(ETH)₂Cl] centre (Ir3B) and a possible [Ir(CO)(ETH)]Cl centre (Ir3A, this appears to have a non-coordinated Cl anion with electron density located in the "anion binding pocket" of the MOF to provide charge balance, although the presence of water in this site cannot be excluded). In addition, SIMU, FLAT and ISOR restraints were used for the refinement of the metalated linker components and the iridium centres. DFIX and EADP restraints were further used to maintain chemically sensible bond lengths for the bridging and ethylene ligands. The data was treated with the SQUEEZE routine available in Platon to account for the large solvent accessible void volumes in the structure.⁸ To account for the removed electron density, 8 ethanol molecules (26e) per formula unit were added to the formula (16 ethanol molecules per unit cell).

SI 5.3 Thermal ellipsoid plots for 1·IrCl



Figure SI 5.1: (left) The asymmetric unit of **1**·IrCl with all non-hydrogen atoms represented by ellipsoids at the 50% probability level (Mn, beige; Ir, orange; Cl, green; C, black; N, blue; O, red; H, white). The structural model includes two disordered bridging ligand components each with a corresponding Ir centre bound to the appropriate pyrazole N-donor. The coordination sphere of one of these iridium centres was refined to include coordinated ethylene and a coordinated chloride anion, while the coordination sphere of the less occupied Ir centre could not be adequately modelled. (right) A perspective view of the metalated site and associated chloride anion (disorder shown) in **1**·IrCl with all non-hydrogen atoms represented by ellipsoids at the 25% probability level. This view displays the disorder of the bridging ligand and associated iridium centres, as described above.

SI 5.4 *F*_{obs} Electron Density Maps for 1·IrCl



Figure SI 5.2: (a) A perspective view of the chelated Ir complex in **1**·IrCl (Ir, orange; Cl, green; C, black; N, blue; O, red) and the overlaid electron density map as viewed from the (b) front, (c) top and (d) side of the complex.

5.6 X-ray crystallography data collection and refinement parameters

Sample	1·lrCl
Crystallographic Parameter	
Formula	$C_{90.9}H_{116.1}Cl_{0.60}Ir_{0.6}Mn_3N_{12}O_{20.6}$
FW	1998.36
Т, К	100(2)
Wavelength, Å	0.71037
Crystal system, space group	P2 ₁ /m
Z	2
a, Å	12.364(3)
b, Å	33.500(7)
c, Å	12.912(3)
α°	90
β <i>,</i> °	97.29(3)
γ°	90
<i>V</i> , Å ³	5304.8(19)
d_{calc} , g/cm ³	1.251
Absorption coefficient, mm ⁻¹	1.181
F(000)	2074
Crystal size, mm ³	$0.28 \times 0.13 \times 0.02$
2θ range for data collection	2.432 to 58.096
Index range	-14 ≤ h ≤ 15, -40 ≤ k ≤ 40, -16
	≤ ≤ 16
Reflections collected	67414
Independent reflections	10667 [R _{int} = 0.0387, R _{sigma} = 0.0223]
Data/restraints/parameters	10667/199/576
GOF on F ²	1.355
Largest diff. peak and hole, eÅ ⁻³	1.71/-0.53
R ₁ , [l>2σ(l)]	$R_1 = 0.0924$, $wR_2 = 0.3047$
wR_2 , all data	$R_1 = 0.1004$, $wR_2 = 0.3129$
CCDC Number	2025173

 Table S2. Crystallographic data collection and refinement parameters for 1·IrCl.

SI 6.0 Adsorption data



Figure SI 6.1: N_2 isotherm data collected on **1**·IrCl at 77 K, after activation from dry pentane at RT for 2 hr. Filled squares represent adsorption, open squares represent desorption.



Figure SI 6.2: N₂ isotherm data collected on $1 \cdot IrBF_4$ at 77K, after activation from dry pentane at RT for 2 hr. Filled circles represent adsorption, open circles represent desorption.

SI 7.0 Nuclear Magnetic Resonance (NMR) data

SI7.1 Time resolved NMR data for ethylene hydrogenation experiments

1·IrCl and **1**·IrBF₄ (~2 mg) were washed with freshly distilled acetone (previously degassed with ethylene) five times under ethylene, allowing the crystals to soak for 1 hr between exchanges. Subsequently, the crystals were washed with distilled pentane (previously degassed with ethylene) five times under ethylene, soaked for 1 hr between each exchange. The sample was pipetted into a pre-weighed NORELL high-pressure NMR tube fitted with a Young's tap under ethylene flow. The excess pentane was removed before the NMR tube was placed under vacuum for 2 hrs. The NMR tube then was dosed with ethylene (1 bar, 105 μ mol) followed by hydrogen (1 bar, 104 μ mol). The NMR tube was sealed and placed in a Varian Gemini 600MHz NMR spectrometer pre-heated to 46°C.

Before the collection the NMR was locked with a benzene (C_6D_6) charged NMR tube at 46 °C, which was then replaced with the pre-loaded high-pressure NMR tube. A T1 delay of 25 s was used. The extent of conversion was calculated by the comparison of the reduction/disappearance in the integral of the alkene CH₂ resonance of ethylene (5.31 ppm) and hydrogen (4.57 ppm), and the appearance of the two CH₃ alkyl resonance of ethane (0.88 ppm). The gas phase chemical shifts are referenced relative to reported data.⁵

S7.2 Sample composition analysis using a CO/CH₄ probe

Samples of **1**-IrCl and **1**-IrBF₄ were activated in a high-pressure NORELL NMR tube using the same protocol described in section S7.1. Following activation, the NMR tube was dosed with a mixture of 1 bar of CH₄ and 1 bar of CO (or 1 bar of CH₄ and 1 bar of H₂ to analyse for ethane). The tube was sealed and transferred to a Varian Gemini 600 MHz NMR.

Exposure to CO/CH₄ results in an instantaneous colour change from yellow to off-white, which, in conjunction with the presence of CO stretching bands in the IR spectrum of the MOF crystals, identifies the major species post CO exposure as $1 \cdot [Ir(CO)_2 CI]$ and $1 \cdot [Ir(CO)_2 BF_4]$ (SI Figure S7.1 and 7.2-7.3). This indicates that ethylene is released into the headspace of NMR tube. Gas-phase NMR spectra of the headspace in the NMR tube revealed the amount of ethylene displaced from the Ir(I) centre (SI Figure 7.4-7.5), via integration of the ethylene and methane signals; the result is consistent with retention of ~84-79% for both samples (slightly more than one equivalent per iridium atom). The amount of ethylene present in the catalyst is 84 mol% ethylene relative to iridium in 1-IrCl (using Energy Dispersive X-ray (EDX) analysis to identify the amount of iridium); the unquantified ligand was considered as CO (i.e. 16 mol% CO relative to iridium in 1·IrCl). This suggests a sample composition of 66% 1·IrCl(ETH) and 34% 1·IrCl(ETH/CO). These results are corroborated by the CO/H₂ experiments (SI Figure 7.6-7.7). The same analysis was conducted in the BF₄ derivative which was found to have 79 mol% ethylene relative to iridium and 21 mol% of CO relative to iridium; this suggests a sample composition of 58% $1 \cdot IrBF_4(ETH)$ and 42% $1 \cdot IrBF_4(ETH/CO)$. The slight reduction in the amount of bis-ethylene complex in the BF₄ sample may be due to enhanced sensitivity of this complex towards ethylene loss due to the charged Ir(I) centre produced by the noncoordinating BF₄ anion, thereby over-estimating the proportion of CO ligated Ir sites in the sample.



Figure SI 7.1: Reaction scheme showing the displacement of the ethylene from the Ir(I) center in **1**·IrCl or **1**·IrBF₄ in presence of CO/CH₄.



Figure SI 7.2: Infra-red spectrum of **1**·IrCl crystals following exposure to CO/CH₄, displaying the strong CO stretches corresponding to the formation of $1 \cdot [Ir(CO)_2 CI]$ as the major product.



Figure SI 7.3: Infra-red spectrum of $1 \cdot IrBF_4$ crystals following exposure to CO/CH₄, displaying the strong CO stretches corresponding to the formation of $1 \cdot [Ir(CO)_2 BF_4]$ as the major product.



Figure SI 7.4: ¹H NMR spectrum obtained from the headspace of an NMR tube containing **1**·IrCl crystals following exposure to CO/CH₄, displaying the ethylene (5.31 ppm) and methane (0.14 ppm) resonances.



Figure SI 7.5: ¹H NMR spectrum obtained from the headspace of an NMR tube containing **1**·IrBF₄ crystals following exposure to CO/CH₄, displaying the ethylene (5.31 ppm) and methane (0.14 ppm) resonances.



Figure SI 7.6: ¹H NMR spectrum obtained from the headspace of an NMR tube containing **1**·IrCl crystals following exposure to H_2/CH_4 , displaying the hydrogen (4.57 ppm), ethane (0.88) and methane (0.14 ppm) resonances.



Figure SI 7.7: ¹H NMR spectrum obtained from the headspace of an NMR tube containing $1 \cdot IrBF_4$ crystals following exposure to H₂/CH₄, displaying the hydrogen (4.57 ppm), ethane (0.88) and methane (0.14 ppm) resonances.

SI 8.0 Infrared (IR) Spectroscopy



Figure SI 8.1: Infra-red spectrum (nujol) of ·IrCl and 1·IrBF₄ crystals before and after hydrogenation catalysis, displaying minor changes in the stretching frequency of CO ligands upon exchange of the chloride anion for BF₄ and following hydrogenation.



Figure SI 8.2: Infra-red spectrum (nujol) of an iridium metalated sample of **1** synthesised in the presence of acetaldehyde (metalation at 65C in ethanol with acetaldehyde) **(B)** and a sample of iridium metalated **1** following exposure to acetaldehyde post-synthesis (**1**·IrCl heated at 65C in ethanol with acetaldehyde) **(A)**. In both samples, strong CO stretches are observed at 2088/2025 cm⁻¹ which indicate the formation of gem dicarbonyl complexes of iridium, supporting the proposal that the decarbonylation of acetaldehyde (generated by ethanol dehydrogenation) is the origin of the CO-ligated by-products present in **1**·IrCl.

SI 9.0 References

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