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# Room Temperature Hydrogenation of CO2 Utilizing a Cooperative Phosphorus Pyridone-Based Iridium Complex 

SIANGWATA, Shepherd, HAMILTON, Alexander, TIZZARD, Graham John, COLES, Simon J. and OWEN, Gareth Richard

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## Supporting Information

Room Temperature Hydrogenation of $\mathrm{CO}_{2}$ Utilizing a Cooperative Phosphorus Pyridone-Based Iridium Complex

Shepherd Siangwata, Alex Hamilton, Graham J. Tizzard, Simon J. Coles, and Gareth R. Owen*

## Supplementary Information for:

# Room Temperature Hydrogenation of $\mathrm{CO}_{2}$ Utilizing a Cooperative Phosphorus Pyridone-Based Iridium Complex 

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## 1. General Remarks

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker 400 MHz Ascend $400\left({ }^{1} \mathrm{H}: 400.13 \mathrm{MHz} ;{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}: 100.62 \mathrm{MHz},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}: 161.97 \mathrm{MHz}\right.$ ) spectrometer. NMR chemical shifts were reported relative to the internal standard tetramethylsilane ( $\delta 0.00$ ). FT-IR spectra were recorded using a PerkinElmer Spectrum Two Attenuated Total Reflectance Infrared spectrometer. The mass spectra were collected at Cardiff University. Elemental analysis was carried out at London Metropolitan University.
2. Synthesis and Characterisation of 2-tbutyloxy-6-bromopyridine


Figure S1 ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of 2-tbutyloxy-6-bromopyridine.

Potassium-tbutoxide ( $1.52 \mathrm{~g}, 13.6 \mathrm{mmol}$ ) was dissolved in dry toluene ( 20 mL ) and added to a stirring solution of 2,6 -dibromopyridine ( $3.22 \mathrm{~g}, 13.6 \mathrm{mmol}$ ) in dry toluene $(40 \mathrm{~mL})$ in a 100 mL Schlenk flask. The reaction mixture was left stirring overnight at $80^{\circ} \mathrm{C}$ under nitrogen atmosphere, and then allowed to cool to room temperature. The mixture was filtered through a wet pad of celite and the solvent in the filtrate was removed under reduced pressure to reveal a white semi-solid crude product. This was then purified by column chromatography, eluting the product using hexane (100\%) as the eluting solvent. Removal of the solvent under reduced pressure and drying in vacuo yielded a clear oil product. Yield: ( $1.64 \mathrm{~g}, 53 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, \delta\right)$ : 7.34 (dd, $\left.{ }^{3} J=8.4 \mathrm{~Hz},{ }^{3} J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{4}\right), 6.97\left(\mathrm{dd},{ }^{3} \mathrm{~J}=7.6 \mathrm{~Hz},{ }^{4} \mathrm{~J}=0.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{5}\right), 6.56$ (dd, $\left.{ }^{3} \mathrm{~J}=8.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}=0.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{3}\right), 1.58\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}_{8}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, \delta\right): 163.0(\mathrm{~s}$, $\mathrm{C}_{6}$ ), 140.0 ( $\mathrm{s}, \mathrm{C}_{4}$ ), 137.6 ( $\mathrm{s}, \mathrm{C}_{2}$ ), 119.5 ( $\mathrm{s}, \mathrm{C}_{3}$ ), 111.4 (s, $\mathrm{C}_{5}$ ), 80.87 ( $\mathrm{s}, \mathrm{C}_{7}$ ), 28.40 ( s , C8). FT-IR ( $V_{\text {max }} / \mathrm{cm}^{-1}$ ): $1586.9(\mathrm{C}=\mathrm{N})$.



Figure $\mathbf{S 2}{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right)$ spectrum of 2-tbutyloxy-6-bromopyridine.

## 3. Synthesis and Characterisation of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine



Figure $\mathrm{S} 3{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ) spectrum of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine.

2-tButyloxy-6-bromopyridine ( $1.04 \mathrm{~g}, 4.52 \mathrm{mmol}$ ) was dissolved in dry THF ( 30 mL ) in a 100 mL Schlenk flask, and the solution was cooled to $-78^{\circ} \mathrm{C}$. To this solution was added n -Butyllithium ( 1.52 M in hexane, $3.27 \mathrm{~mL}, 4.97 \mathrm{mmol}$ ) dropwise (over 30 min ) and the reaction was allowed to continue stirring for 3 hours at $-78^{\circ} \mathrm{C}$. Chlorodicyclohexylphosphine ( $1.16 \mathrm{~g}, 4.97 \mathrm{mmol}$ ) was dissolved in dry THF ( 30 mL ) and then cannulated to the stirring solution. The reaction was left stirring to room temperature overnight under nitrogen, after which distilled water ( 15 mL ) was added, and the organic solvent was removed under reduced pressure. An extraction was carried out with ethyl acetate and the organic layer was washed with distilled water,
brine and then filtered over magnesium sulfate. The filtrate was further purified by column chromatography ( $100 \%$ DCM), eluting the product as a clear oil which was collected and dried in vacuo. Yield: ( $1.14 \mathrm{~g}, 72 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, \delta\right): 7.33$ (ddd, ${ }^{3} \mathrm{~J}=$ $\left.8.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}=7.1 \mathrm{~Hz},{ }^{4} \mathrm{JHP}=2.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{4}\right), 6.98\left(\mathrm{td},{ }^{3} \mathrm{~J}=7.0 \mathrm{~Hz},{ }^{4} \mathrm{~J}=0.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{3}\right)$, 6.46 (ddd, $\left.{ }^{3} \mathrm{~J}=8.3 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HP}}=8.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}=1.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{5}\right), 2.09-1.98\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{H}_{7}\right)$, 1.84-1.75 (m, 2H, Hcy), 1.75-1.66 (m, 2H, Hcy), 1.62-1.55 (m, 4H, Hcy), 1.54 (s, 9H, $\left.\mathrm{H}_{12}\right), 1.51-1.45\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Hcy}^{\prime}\right), 1.24-0.90\left(\mathrm{~m}, 10 \mathrm{H}, \mathrm{Hcy}_{\mathrm{c}}\right) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, \delta\right): 163.4$ (d, ${ }^{3}{ }^{J} \mathrm{PC}=3.6 \mathrm{~Hz}, \mathrm{C}_{2}$ ), 137.1 (d, $\left.{ }^{1} \mathrm{JPC}=23 \mathrm{~Hz}, \mathrm{C}_{6}\right), 125.2$ (d, $\left.{ }^{3} \mathrm{JPC}_{\mathrm{PC}}=4.2 \mathrm{~Hz}, \mathrm{C}_{4}\right), 112.8$ (d, ${ }^{2}{ }^{\text {JPC }}=10 \mathrm{~Hz}, \mathrm{C}_{5}$ ), 79.18 (s, C 3 ), 32.77 (br s, Cy), 29.85 (d, JPC = $13.7 \mathrm{~Hz}, \mathrm{Cy}$ ), 29.35 (br s, Cy), 29.73 (s, C 12 ), 28.58 (s, C 11 ), 27.25 (d, JPC $=11.9 \mathrm{~Hz}, \mathrm{Cy}$ ), 26.97 (d, JPC $=$ $8.2 \mathrm{~Hz}, \mathrm{Cy}), 26.41$ (br s, Cy). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.\mathrm{CDCl}_{3}, \delta\right): 8.39$ (s). FT-IR ( $\mathrm{Vmax}^{2} / \mathrm{cm}^{-1}$ ): 1563.7 (C=N). Elemental Anal. Calcd. For: $\mathrm{C}_{21} \mathrm{H}_{34}$ NOP, (\%) C: 72.59, H: 9.86, N: 4.03, Found (\%) C: 72.68, H: 9.63, N: 3.78. ESI-MS (positive ion-mode), $(\mathrm{m} / \mathrm{z})=348.25$ [M + H] ${ }^{+}$(calcd. 348.25).


Figure S4 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine.


Figure $\mathbf{S 5}{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine.


Figure S6 ESI-MS fragmentation pattern of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine.


Figure S7 FT-IR spectrum of 2-tbutyloxy-6-dicyclohexylphosphinylpyridine.
4. Synthesis and Characterisation of 6-dicyclohexylphosphino-2-pyridone (6DCyPPon)


Figure $\mathbf{S 8}{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ) spectrum of 6-dicyclohexylphosphino-2-pyridone (6-D ${ }^{\text {CyPPon }}$ ).

Formic acid ( 15 mL , concentrated) was added dropwise to a 100 mL Schlenk flask containing 2-tbutyloxy-6-dicyclohexylphosphinylpyridine ( $1.38 \mathrm{~g}, 3.97 \mathrm{mmol}$ ) kept under nitrogen atmosphere. The reaction was left stirring at room temperature for 4 h , after which distilled water ( 25 mL ) was added, revealing a milky-white solution. The solution was transferred to a separating funnel for extraction using DCM. The organic extracts were combined and washed with brine, then dried over $\mathrm{MgSO}_{4}$ and filtered by gravity. The solvent in the filtrate was removed under reduced pressure, and residual formic acid was removed via azeotropic distillation with ethanol, revealing a white solid product which was collected and dried in vacuo. Yield: ( $1.02 \mathrm{~g}, 88 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$, ס): 9.40 (br s, 1H, H $\mathrm{H}_{1}$, 7.35 (ddd, $\left.{ }^{3} \mathrm{~J}=9.2 \mathrm{~Hz},{ }^{3} \mathrm{~J}=6.6 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HP}}=1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{4}\right), 6.55$ (dt, ${ }^{3} \mathrm{~J}=9.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}=1.1 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{3}$ ), $6.38\left(\mathrm{ddd},{ }^{3} \mathrm{~J}=6.8 \mathrm{~Hz},{ }^{3} \mathrm{JHP}=6.0 \mathrm{~Hz},{ }^{4} \mathrm{~J}=1.2 \mathrm{~Hz}\right.$, 1H, H5), 1.98-1.87 (m, 2H, Hcy), 1.87-1.75 (m, 4H, Hcy), 1.70-1.56 (m, 6H, Hcy), 1.351.10 (m, 10H, Hcy). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.\mathrm{CDCl}_{3}, \delta\right): 163.4$ (s, C $\mathrm{C}_{2}$ ), 144.7 (d, ${ }^{1} \mathrm{~J}$ PC $=35.3 \mathrm{~Hz}$, $\left.\mathrm{C}_{6}\right), 139.2\left(\mathrm{~d},{ }^{3} \mathrm{JPC}_{\mathrm{PC}}=8.6 \mathrm{~Hz}, \mathrm{C}_{4}\right), 120.0\left(\mathrm{~s}, \mathrm{C}_{3}\right), 114.4\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PC}}=23.1 \mathrm{~Hz}, \mathrm{C}_{5}\right), 31.46(\mathrm{~d}$, $\left.J_{\mathrm{PC}}=12.1 \mathrm{~Hz}, \mathrm{Cy}\right), 29.12$ (d, JPC = $17.2 \mathrm{~Hz}, \mathrm{Cy}$ ), 28.26 (d, JPC = $7.1 \mathrm{~Hz}, \mathrm{Cy}$ ), 25.90 (d, $\left.J_{\mathrm{PC}}=12.9 \mathrm{~Hz}, \mathrm{Cy}\right), 25.69$ (d, JPC $\left.=7.7 \mathrm{~Hz}, \mathrm{Cy}\right), 25.14$ (d, JPC $\left.=1.0 \mathrm{~Hz}, \mathrm{Cy}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.\mathrm{CDCl}_{3}, \delta\right): 2.99(\mathrm{~s})$. FT-IR ( $\mathrm{v}_{\mathrm{max}} / \mathrm{cm}^{-1}$ ): $2855.8(\mathrm{~N}-\mathrm{H})$, $1648.8(\mathrm{C}=\mathrm{O})$. Elemental Anal. Calcd. For: $\mathrm{C}_{17} \mathrm{H}_{26}$ NOP, (\%) C: 70.08, H: 8.99, N: 4.81, Found (\%) C: 69.65, H: 8.96, N: 4.49. ESI-MS (positive ion-mode), $(\mathrm{m} / \mathrm{z})=292.18[\mathrm{M}+\mathrm{H}]^{+}$(calcd. 292.18).

$\stackrel{8}{i}$


Figure S9 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of 6-dicyclohexylphosphino-2-pyridone (6-D ${ }^{\text {Cy }} \mathrm{PPon}$ ).


Figure $\mathbf{S 1 0}{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of 6-dicyclohexylphosphino-2-pyridone (6-D ${ }^{\text {CyPPon }}$ ).


Figure S11 FT-IR spectrum of 6-dicyclohexylphosphino-2-pyridone (6-D ${ }^{\text {CyPPon }}$ ).


Figure S12 ESI-MS fragmentation pattern of 6-dicyclohexylphosphino-2-pyridone (6-D ${ }^{\text {CyPPon }}$ ).
5. Synthesis and Characterisation of $\left.\left[\operatorname{Ir}\left(K^{2}-P, N-6-D^{C y} P o\right)^{*}\right)(C O D)\right](1)$




Figure S13 ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of $\left[\operatorname{lr}\left(\kappa^{2}-P, N-6-D^{\text {CyPPon* }}\right)(\mathrm{COD})\right](1)$.

6-Dicyclohexylphosphinylpyridone ( $0.250 \mathrm{~g}, 0.859 \mathrm{mmol}$ ) was dissolved in dry DCM ( 10 mL ) under nitrogen atmosphere, and added dropwise to a stirring solution of
iridium dimer [ $\mathrm{Ir}(\mathrm{COD}) \mathrm{OMe}]_{2}(0.285 \mathrm{~g}, 0.429 \mathrm{mmol})$ in DCM $(10 \mathrm{~mL})$. The solution was left stirring overnight at room temperature under nitrogen atmosphere. The solvent of the reaction was then removed in vacuo to reveal a reddish-orange solid product which was collected and dried in vacuo. Yield: ( $0.458 \mathrm{~g}, 90 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}, \delta$ ): 7.10 (ddd, $\left.{ }^{3} \mathrm{~J}_{\mathrm{HH}}=9.1 \mathrm{~Hz},{ }^{3} \mathrm{JHH}=6.5 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HP}}=3.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{H}_{4}\right), 6.38\left(\mathrm{dd},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=9.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=0.8\right.$ $\mathrm{Hz}, 1 \mathrm{H}, \mathrm{H}_{3}$ ), $5.89\left(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{H}_{11}\right.$ ',trans-P), $5.73\left(\mathrm{ddd},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.4 \mathrm{~Hz},{ }^{3} \mathrm{~J}_{\mathrm{HP}}=5.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=\right.$
 ( $\mathrm{m}, 12 \mathrm{H}, \mathrm{H}_{12+12{ }^{\prime}+\mathrm{cy}}$ ), 1.57-1.44 (m, 2H, Hcy), 1.30-1.03 (m, 8H, Hcy). ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, \delta\right): 169.2\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{PC}}=14 \mathrm{~Hz}, \mathrm{C}_{2}\right), 162.6\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{PC}}=53.5 \mathrm{~Hz}, \mathrm{C}_{6}\right), 135.6\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{PC}}=\right.$ $\left.7.9 \mathrm{~Hz}, \mathrm{C}_{4}\right), 120.6\left(\mathrm{~d},{ }^{4} \mathrm{~J}_{\mathrm{PC}}=2.5 \mathrm{~Hz}, \mathrm{C}_{3}\right), 109.8\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PC}}=3.1 \mathrm{~Hz}, \mathrm{C}_{5}\right), 88.01\left(\mathrm{~d},{ }^{2}{ }^{\mathrm{JPC}}=\right.$ $10.6 \mathrm{~Hz}, \mathrm{C}_{\text {cod-11',trans-P), }} 55.24$ ( $\mathrm{s}, \mathrm{C}_{\text {cod-11,trans-N), }} 31.83$ (d, JPC $=3.0 \mathrm{~Hz}, \mathrm{C}_{\text {cod-12,trans-N) }}$ ), 30.27 (d, ${ }^{2}{ }^{\mathrm{JPC}}=23.3 \mathrm{~Hz}, \mathrm{C}_{7}$ ), 29.77 (d, Jpc = $1.4 \mathrm{~Hz}, \mathrm{Cy}$ ), 28.16 (d, ${ }^{1} \mathrm{Jpc}=3.4 \mathrm{~Hz}, \mathrm{Cy}$ ), 27.94 (s, C Cod-12',trans-P), 25.65 (dd, JPC $=16.56 \mathrm{~Hz}, J_{\text {PC }}=13.94 \mathrm{~Hz}, \mathrm{Cy}$ ), 24.94 (s, Cy). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, \delta\right):-31.53(\mathrm{~s})$. FT-IR $\left(v_{\mathrm{max}} / \mathrm{cm}^{-1}\right)$ : 1622.3 (C=O). Elemental Anal. Calcd. For: $\mathrm{C}_{25} \mathrm{H}_{3} 7 \mathrm{NOPIr},(\%) \mathrm{C}: 50.83, \mathrm{H}: 6.31, \mathrm{~N}: 2.31$, Found (\%) C: 50.17, H: 6.04, N : 2.90. ESI-MS (positive ion-mode), $(\mathrm{m} / \mathrm{z})=592.23[\mathrm{M}+\mathrm{H}]^{+}$(calcd. 592.22).


Figure S14 ${ }^{31}{ }^{1}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of $\left[\mathrm{Ir}\left(\mathrm{k}^{2}-\mathrm{P}, \mathrm{N}-6-\mathrm{D}^{\mathrm{Cy}} \mathrm{Pon}{ }^{*}\right)(\mathrm{COD})\right]$ (1).


Figure S15 ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ spectrum of $\left[\operatorname{lr}\left(\mathrm{K}^{2}-P, N-6-\mathrm{D}^{\text {CyPon }}{ }^{*}\right)(\mathrm{COD})\right](1)$.


Figure S16 FT-IR spectrum of [Ir( $\mathrm{K}^{2}-P, N-6-\mathrm{D}^{\text {CyP }}{ }^{\text {Pon }}$ * (COD) $]$ (1).


Figure S17 ESI-MS fragmentation pattern of [Ir( $\left.\left.\kappa^{2}-P, N-6-D^{\text {CyPon }}{ }^{*}\right)(C O D)\right]$ (1).

## 6. Catalytic hydrogenation of $\mathrm{CO}_{2}$ to formate salt using complex 1

In a nitrogen filled glovebox, complex $1\left(5.90 \times 10^{-3} \mathrm{~g}, 0.010 \mathrm{mmol}\right.$ or $9.8 \times 10^{-4} \mathrm{~g}$, $1.66 \times 10^{-3} \mathrm{mmol}$ ), DBU (between $0-10,000$ equivalents) [see Table S 1 below for details on each run], and THF ( 5 mL ) were added to a 50 mL high-pressure autoclave reactor equipped with a magnetic stirrer bar. The charged reactor was then placed in the fume hood and pressurised with $\mathrm{CO}_{2}$ gas while stirring to reach the equilibration pressure. This is to allow the DBU within the mixture to react to form the $\mathrm{DBU} \cdot \mathrm{CO}_{2}$ adduct. ${ }^{[17]}$ This was followed by $\mathrm{H}_{2}$ gas and stirred at the room temperature of the laboratory ( $20^{\circ} \mathrm{C} \pm 2{ }^{\circ} \mathrm{C}$ ). After stirring for the desired time, the pressure in the reactor was carefully released. DMF (equimolar to DBU) was then added as an internal standard into the reaction mixture. The reaction mixture was then analysed by ${ }^{1} \mathrm{H}$ NMR with a few drops of $\mathrm{D}_{2} \mathrm{O}$ to lock the signals.

Table S1 Showing quantities of catalyst and base used for the experiments.

| Entry $^{\text {a }}$ | Catalyst |  | DBU |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | mmol | mass | equiv. | mmol | Mass |
| $1-3$ | 0.01 mmol | $5.9 \times 10^{-3} \mathrm{~g}$ | 500 | 5.00 mmol | 0.7612 g |
| 4 | 0.01 mmol | $5.9 \times 10^{-3} \mathrm{~g}$ | 0 | 0 | 0 |
| 5 | 0.01 mmol | $5.9 \times 10^{-3} \mathrm{~g}$ | 5000 | 50.00 mmol | 7.612 g |
| $6^{b} \& 7^{b}$ | $1.66 \times 10^{-3} \mathrm{mmol}$ | $9.8 \times 10^{-4} \mathrm{~g}$ | 10000 | 16.66 mmol | 2.5373 g |

${ }^{a}$ All entries correlate with Table 1 in main article. ${ }^{b}$ The reactions involving 10000 equiv., were carried out on a six-fold lower scale (quantities divided by 6 ), with the exception of THF, to circumvent requirement for large quantities of DBU base.


Figure S 18 A representative ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{D}_{2} \mathrm{O}\right)$ spectrum of a crude catalytic reaction mixture used for computing the TON (table 1, entry 2 in main article).

## 7. High pressure NMR spectroscopy studies: reactivity of complex 1 with $\mathbf{H}_{2}$

Complex $1\left(5.9 \times 10^{-3} \mathrm{~g}, 0.01 \mathrm{mmol}\right)$ was dissolved in benzene-d $6(0.3 \mathrm{~mL})$ in a highpressure NMR tube, which was then pressurised with 1 bar $\mathrm{H}_{2}$ and spectra were recorded for ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR within 10 minutes. The NMR tube was then placed under vacuum to remove the $\mathrm{H}_{2}$ in the headspace, and filled with nitrogen atmosphere and then spectra were recorded over time.


Figure S19 Stacked ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectra of 1 illustrating room temperature reversible reactivity with $\mathrm{H}_{2}$.


Figure S20 Stacked selected regions of ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectra of 1 illustrating room temperature reversible reactivity with $\mathrm{H}_{2}$.

|  | NH | $\mathrm{H}_{4}$ | $\mathrm{H}_{3}$ | $\mathrm{H}_{5}$ | $\mathrm{H}_{11}$ | $\mathrm{H}_{11}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Complex 1 | n/a | $6.89(\mathrm{~m})$ | $6.83(\mathrm{~m})$ | $5.38(\mathrm{~m})$ | $6.64(\mathrm{br}$ s $)$ | $3.84(\mathrm{br} . \mathrm{s})$ |
| Complex 2 | $11.23(\mathrm{~s})$ | $6.65(\mathrm{~m})$ | $6.53(\mathrm{~m})$ | $5.75(\mathrm{br} . \mathrm{s})$ | $4.34(\mathrm{~s})$ | $3.58(\mathrm{~s})$ |

 \# = DCM


Figure S21 Full range stacked ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectra illustrating room temperature reactivity of complex 1 with $\mathrm{H}_{2}$ to form complex 2. Inset table: showing differences in chemical shifts of complexes 1 and 2.

+1 Bar $\mathrm{H}_{2}, \mathrm{~T}=10 \mathrm{~min}$ ． （complex 2）．


Figure S22 Stacked ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ spectra illustrating room temperature reactivity of complex 1 with $\mathrm{H}_{2}$ to form complex 2.

## 8. Crystallographic data collection, reduction, and structure solution refinement

CCDC number 2309375, (NCS 2023ncs0208r1), contain supplementary crystallographic data for complex 1 . This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

## Details for complex 1

Single orange block-shaped crystals of 1 were obtained by recrystallisation from a concentrated THF solution. A suitable crystal $0.15 \times 0.10 \times 0.09 \mathrm{~mm}^{3}$ was selected and mounted on a MITIGEN holder in oil on a Rigaku FRE+ diffractometer with Arc) Sec VHF Varimax confocal mirrors, a UG2 goniometer and HyPix 6000HE detector. The crystal was kept at a steady $T=100(2) \mathrm{K}$ during data collection. The data was processed using the CrysAlisPro 1.171.42.94a program. ${ }^{[18]}$ The structure was solved with the ShelXT 2018/2 ${ }^{[19]}$ structure solution program using the using dual methods solution method and by using Olex2 $1.5-$ alpha $^{[20]}$ as the graphical interface. The model was refined with olex2.refine 1.5-alpha ${ }^{[21]}$ using full matrix least squares minimisation on $F^{2}$ minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.
Additional refinement details: The COD ligand has been modelled as partially disordered (56:44). 1,2 and 1,3 equal distance geometrical restraints have been applied to all equivalent atom pairs of the disorder components.
Experimental absorption process details: CrysAlisPro 1.171.42.94a (Rigaku OD, 2023) using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.


Figure S23 Crystal structure of [Ir( $\left.\left.\mathrm{K}^{2}-P, N-6-\mathrm{D}^{\text {Cy }} \mathrm{Pan}^{*}\right)(\mathrm{COD})\right]$ (1), highlighting disorder in the COD unit. The minor component is in grey.

Table S1 X-ray data collection parameters for complex 1.

| Compound | 1 |
| :---: | :---: |
| CCDC No: | 2309375 |
| Formula | $\mathrm{C}_{25} \mathrm{H}_{37} \mathrm{IrNOP}$ |
| Dcalc./ $\mathrm{g} \mathrm{cm}^{-3}$ | 1.715 |
| $\mu / m^{-1}$ | 5.920 |
| Formula Weight | 590.768 |
| Colour | orange |
| Shape | block-shaped |
| Size/mm ${ }^{3}$ | $0.15 \times 0.10 \times 0.09$ |
| T/K | 100(2) |
| Crystal System | monoclinic |
| Space Group | P21/n |
| $a / A$ | 10.3796(1) |
| $b / A$ | 16.1116(1) |
| $c / \AA$ | 14.0850(1) |
| $\alpha /^{\circ}$ | 90 |
| $\beta /{ }^{\circ}$ | 103.693(1) |
| ${ }^{\prime \prime}$ | 90 |
| V/ $\AA^{3}$ | 2288.52(3) |
| Z | 4 |
| Z' | 1 |
| Wavelength/A | 0.71075 |
| Radiation type | Mo K ${ }_{\alpha}$ |
| $Q_{\text {min }} /{ }^{\circ}$ | 1.95 |
| $Q_{\text {max }} /{ }^{\circ}$ | 36.18 |
| Measured Refl's. | 181325 |
| Indep't Refl's | 10543 |
| Refl's $\mathrm{l} \geq 2 \mathrm{~s}$ (I) | 9721 |
| $R_{\text {int }}$ | 0.0416 |
| Parameters | 299 |
| Restraints | 30 |
| Largest Peak | 1.5069 |
| Deepest Hole | -1.0295 |
| GooF | 1.0456 |
| $w R_{2}$ (all data) | 0.0406 |
| wR2 | 0.0395 |
| $R_{1}$ (all data) | 0.0236 |
| $R_{1}$ | 0.0194 |
| Flack Parameter | - |
| Hooft Parameter | - |

Table S2 Selected bond distances $(\AA)$ for complex 1.

| Atom | Atom | Length $/$ A |
| :---: | :---: | :---: |
| Ir1 | P1 | $2.2975(3)$ |
| Ir1 | N1 | $2.0768(12)$ |
| Ir1 | C7a | $2.117(8)$ |
| Ir1 | C10 | $2.1864(14)$ |
| Ir1 | C11 | $2.1757(15)$ |
| Ir1 | C14a | $2.138(5)$ |
| P1 | C6 | $1.8284(14)$ |
| P1 | C15 | $1.8340(13)$ |
| P1 | C21 | $1.837(14)$ |
| O1 | C2 | $1.2412(18)$ |
| N1 | C2 | $1.3946(17)$ |
| N1 | C6 | $1.3801(18)$ |
| C2 | C3 | $1.452(2)$ |
| C3 | C4 | $1.362(2)$ |
| C4 | C5 | $1.419(2)$ |
| C5 | C6 | $1.3661(19)$ |
| C7a | C8a | $1.521(8)$ |
| C7a | C14a | $1.423(8)$ |
| C8a | C9 | $1.528(4)$ |
| C9 | C10 | $1.515(2)$ |
| C10 | C11 | $1.396(2)$ |
| C11 | C12 | $1.510(3)$ |
| C12 | C13a | $1.535(4)$ |
| C13a | C14a | $1.515(6)$ |

Numbering scheme is used as received from the crystallography data (see Figures 3 and 4 in main article).

Table S3 Selected bond angles $\left({ }^{\circ}\right)$ for complex 1.

| Atom | Atom | Atom | Angle/ ${ }^{\circ}$ |
| :---: | :---: | :---: | :---: |
| N1 | Ir1 | P1 | 69.13(3) |
| C7a | Ir1 | P1 | 105.4(2) |
| C7a | Ir1 | N1 | 163.67(15) |
| C10 | Ir1 | P1 | 161.45(5) |
| C10 | Ir1 | N1 | 99.15(5) |
| C10 | Ir1 | C7a | 81.8(2) |
| C11 | Ir1 | P1 | 155.52(5) |
| C11 | Ir1 | N1 | 100.26(5) |
| C11 | Ir1 | C7a | 90.35(19) |
| C11 | Ir1 | C10 | 37.32(6) |
| C14a | Ir1 | P1 | 98.06(12) |
| C14a | Ir1 | N1 | 154.32(13) |
| C14a | Ir1 | C7a | 39.07(19) |
| C14a | Ir1 | C10 | 98.05(13) |
| C14a | Ir1 | C11 | 82.31(14) |
| C6 | P1 | Ir1 | 84.13(4) |
| C15 | P1 | Ir1 | 123.26(5) |
| C15 | P1 | C6 | 110.29(6) |
| C21 | P1 | Ir1 | 119.44(5) |
| C21 | P1 | C6 | 110.06(6) |
| C21 | P1 | C15 | 106.65(6) |
| C2 | N1 | Ir1 | 133.13(10) |
| C6 | N1 | Ir1 | 105.63(8) |
| C6 | N1 | C2 | 120.91(12) |
| N1 | C2 | 01 | 121.44(13) |
| C3 | C2 | 01 | 123.25(13) |
| C3 | C2 | N1 | 115.30(12) |
| C4 | C3 | C2 | 122.40(13) |
| C5 | C4 | C3 | 120.58(13) |
| C6 | C5 | C4 | 116.76(13) |
| N1 | C6 | P1 | 100.77(9) |
| C5 | C6 | P1 | 135.18(11) |
| C5 | C6 | N1 | 124.01(12) |
| C8a | C7a | Ir1 | 113.3(4) |
| C14a | C7a | Ir1 | 71.3(4) |
| C14a | C7a | C8a | 123.4(5) |
| C9 | C8a | C7a | 114.9(4) |
| C10 | C9 | C8a | 112.39(17) |
| C10 | C9 | C8b | 116.83(18) |
| C9 | C10 | Ir1 | 110.37(10) |
| C11 | C10 | Ir1 | 70.93(9) |
| C11 | C10 | C9 | 124.66(16) |
| C10 | C11 | Ir1 | 71.76(9) |
| C12 | C11 | Ir1 | 110.89(11) |
| C12 | C11 | C10 | 125.21(16) |
| C13a | C12 | C11 | 115.99(17) |
| C14a | C13a | C12 | 112.7(3) |
| C7a | C14a | Ir1 | 69.7(3) |
| C13a | C14a | Ir1 | 111.3(3) |
| C13a | C14a | C7a | 124.4(4) |

Numbering scheme is used as received from the crystallography data (see Figures 3 and 4 in main article).

## 9. Computational Details

All DFT calculations undertaken using the ORCA 4.2.1 computational software. ${ }^{[22]}$ Optimisations and analytical frequency calculations were performed at the B97-D3/def2-TZVP level of theory ${ }^{[23-25]}$ with further solvated energy evaluations at the RIJCOSX-wB97M-V/def2-tzvpp level of theory, ${ }^{[26,27]}$ for calculation of the solvation free energy differences. All calculation included the Resolution of Identity approximation to reduce computational cost. ${ }^{[28]}$ Solvation correction was implemented with the SMD model derived to represent benzene and THF environments. ${ }^{[29]}$ Numerical precision integration grids were increase beyond the default settings, during optimisations to Grid4 for the SCF step Grid5 for the final energy evaluation, and further to Grid6 for the NMR calculations. NMR predictions were calculated with the TPSSh functional, ${ }^{[30]}$ with the specially derived NMR specific pcS-2 basis set by Jensen. ${ }^{[31]}$ This choice of methodology has been shown to give good predictions at an affordable computational expense. ${ }^{[32]}$ Due to the relativistic nature of iridium the SARC-ZORA-TZVPP basis set was used for the metal centre. ${ }^{[33]}$ Calculations not accounting for relativistic effects did not give reliable predictions.

Graphical visualisation and structural analysis performed from the DFT calculations using Avogadro 1.2.0. ${ }^{[34]}$

## ORCA - xyz coordinates for Complex 2

| Ir | -3.01217187798878 | -1.85481455874740 | -2.07115335151942 |
| :--- | :---: | :--- | :--- |
| P | -0.96320937318143 | -2.70493821873981 | -2.48602538107660 |
| C | -0.47886311118750 | -2.93592268634846 | -4.23455966733109 |
| C | -0.62611528815187 | -4.35223689959411 | -1.75293502742202 |
| H | -1.23353341672822 | -3.58314056014649 | -4.68833270260594 |
| H | 0.50626736117256 | -3.40090301761486 | -4.33212056183354 |
| H | -0.49144252467817 | -1.97486904548892 | -4.75345309898109 |
| H | -1.34228498327793 | -5.06581710053697 | -2.16983020811526 |
| H | -0.78524108810335 | -4.29286827798339 | -0.67378791175583 |
| H | 0.39809171345955 | -4.67518060612439 | -1.96273258722841 |
| N | 0.18824230045862 | -1.20139476000055 | -0.53692589320014 |
| C | 0.41985818802496 | -1.70927154846786 | -1.77956051178001 |
| C | 1.62704861206434 | -1.47063795202282 | -2.38696703266711 |
| H | 1.83980160067984 | -1.86296433336540 | -3.37243192330654 |
| C | 2.59632708282456 | -0.69416506968482 | -1.69292584486919 |
| H | 3.55343074501299 | -0.49904190291801 | -2.17289919469675 |
| C | 2.34871640568102 | -0.18881923478766 | -0.44712308507060 |


| Н | 3.07782084321750 | 0.41420786901533 | 0.08369417358115 |
| :--- | :--- | :--- | :--- |
| С | 1.07885917830653 | -0.40534706398590 | 0.22131519506757 |
| О | 0.73650519410837 | 0.03347670230389 | 1.31498574891906 |
| С | -4.44154312745919 | 0.23995812911326 | -0.26937746233292 |
| С | -3.47485486414800 | 1.13692002830482 | -1.07012170992171 |
| С | -2.49695567290710 | 0.36901482474256 | -1.95072392282578 |
| С | -2.75269535664488 | 0.03414529965932 | -3.29006596425004 |
| Н | -1.45379928605729 | 0.46444294107985 | -1.66741972265111 |
| Н | -1.88675879213400 | -0.07488259763905 | -3.94070665739197 |
| С | -4.78258558348784 | -1.06958479749005 | -0.95020643577218 |
| С | -4.03858062938738 | 0.34007252207923 | -4.03121402322170 |
| С | -5.15475110552359 | -1.20039429085533 | -2.29931411615027 |
| Н | -4.05933580712780 | 1.40320816500243 | -4.32200933801399 |
| С | -5.31557954022993 | -0.01536571472069 | -3.24393408415628 |
| Н | -4.02781815961640 | -0.23765911110488 | -4.96112756971547 |
| Н | -6.11738348183505 | -0.24312922439917 | -3.95448718712527 |
| Н | -5.65921533665384 | 0.85114171900495 | -2.66901105703263 |
| Н | -5.10508539791852 | -1.85679258619664 | -0.27360810337877 |
| Н | -5.71883652265385 | -2.08919115855001 | -2.56339559556626 |
| Н | -5.37022877728682 | 0.78922908730657 | -0.04383698725152 |
| Н | -3.98051553877648 | -0.00105312978929 | 0.69310106094700 |
| Н | -2.90064760214415 | 1.74849161519900 | -0.36648547427647 |
| Н | -4.03853879470890 | 1.84134844009432 | -1.69169917484626 |
| Н | -3.47969934147413 | -3.33872978526022 | -1.67480136199273 |
| Н | -0.75269728976822 | -1.31628601243374 | -0.15091601103458 |
| Н | -2.50795408052030 | -1.85833807800665 | -0.47879683709288 |
| Н | -3.40090768634983 | -2.42990818850194 | -3.56807448885436 |

## 10. References

The numbering of these references carries on from the numbering in the main article.
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