

Supporting information for the paper:

A Simple, General Route to 2-Pyridylidene Transition Metal Complexes

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Crystallographic data are also deposited with Cambridge Crystallographic Data Centre. Copies of the data (**3b**, **5b**: CCDC 791629 and 791630) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CD 1EZ, UK; fax +44 1223 336033.

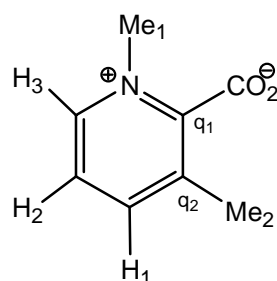
General. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained from Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400 and DPX-300 spectrometers. Spectra were referenced to external SiMe₄ (δ 0 ppm) using the residual protio solvent peaks as internal standards (¹H NMR experiments) or the characteristic resonances of the solvent nuclei (¹³C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free argon, following conventional Schlenk techniques. 3-methylpyridine-2-carboxylic acid was purchased

from Apollo Scientific. N-methyl-2-carboxypyridinium betaine **1a**,¹ [RhCl(cod)],² [IrCl(cod)],³ [AuCl(SMe₂)]⁴ and [PtCl₂(dmsO)₂]⁵ were prepared according to literature procedures. Pyridinium 2-carboxylate **1c** has been prepared following Katritzky's procedure.⁶

2. Synthesis and spectroscopic and analytical data for new compounds.

Synthesis of 1,3-dimethyl-2-carboxypyridine (**1b**)

400 mg (3.6 mmol) of Na₂CO₃ are added to a solution of 1g (7.3 mmol) of 3-methylpyridine-2-carboxylic acid in 5 mL of methanol. The mixture is stirred at room temperature for 1.5 hours to yield a colorless solution that is then cooled to -60 °C and treated with 880 μL (7.3 mmol) of methyl triflate. After 30 minutes the solution is brought to room temperature and the solvent is removed *in vacuo*. The resulting white solid, which contains sodium triflate, is charged on a 10x2 cm silica gel column, the salt being eluted with acetone (100 mL) and the carboxypyridine **1b** with a CH₂Cl₂/methanol 1:1 mixture. Solvent is removed *in vacuo* to yield 930 mg (84% yield) of a white highly hygroscopic solid. This compound is dissolved in the minimum amount of methanol and dried with activated molecular sieves for a period of two days to remove all traces of water. The solvent is then removed *in vacuo* and the white solid stored in a glove-box.



IR (nujol): ν (CO₂) 1640 cm⁻¹.

¹H NMR (400 MHz, d₆-dmsO): δ = 8.55 (d, 1H, ³J_{HH} = 6.2, H₃), 8.28 (d, 1H, ³J_{HH} = 7.7, H₁), 7.72 (dd, 1H, ³J_{HH} = 7.7 and 6.2 Hz, H₂), 4.16 (s, 3H, N-Me), 2.37 (s, 3H, C-Me).
¹³C {¹H} NMR (100 MHz, d₆-dmsO): δ = 161.5 (CO₂), 155.9 (C_{q1}), 145.5 (CH²), 141.1 (CH³), 132.7 (CH¹), 123.6 (C_{q2}), 45. (N-Me), 17.65 (Me).

¹ H Quast and E. Schmitt, *Liebigs Ann. Chem.*, 1970, **732**, 64.

² G. Giordano and R.H.Crabtree, *Inorg. Synth.*, 1990, **28**, 88.

³ J.L. Herde, L.C. Lambert and C.V. Senoff, *Inorg. Synth.*, 1974, **15**, 18.

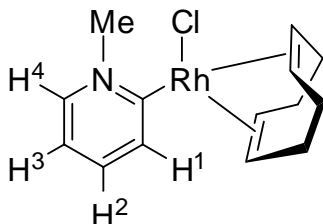
⁴ T.N. Hooper, C.P. Butts, M. Green, M.F. Haddow, J.E. McGrady and C.A. Russell, *Chem.–Eur.J.*, 2009, **15**, 12196.

⁵ V.Y. Kukushkin, A.J.L. Pombeiro, C.M.P. Ferreira and L.I. Elding, *Inorg. Synth.*, 2002, **33**, 192.

⁶ A.R. Katritzky, R. Awartani and R.C. Patel, *J. Org. Chem.*, 1982, **47**, 498.

Anal. Calcd for C₈H₉NO₂: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.2; H, 5.9; N, 9.3.

Synthesis of complex **2a**.



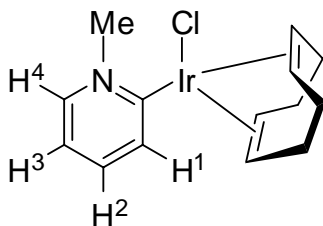
A suspension of 40 mg (0.29 mmol) of N-methyl-2-carboxypyridine, **1a**, and 72 mg (0.15 mmol) of [RhCl(cod)]₂ in 2 mL of dry THF is heated at 65°C for 2 hours under inert atmosphere. The dark red solution is filtered *via* cannula. Addition of 5 mL of pentane to the resulting solution yields a yellow precipitate that is further washed with 2 mL of pentane. The solid is dried *in vacuo* to yield 69 mg of **2a** (70% yield).

¹H NMR (500 MHz, CDCl₃): δ = 8.15 (d, 1H, ³J_{HH} = 8.4 Hz, H¹), 8.00 (d, 1H, ³J_{HH} = 6.4 Hz, H⁴), 7.22 (dd, 1H, ³J_{HH} = 8.4 and 6.4 Hz, H²), 6.91 (m, 1H, H³), 5.00 (m, 2H, =CH_{cod}), 4.80 (s, 3H, N-Me), 3.24 (m, 1H, =CH_{cod}), 3.11 (m, 1H, =CH_{cod}), 2.52-2.22 (m, 4H, CH₂), 2.05-1.84 (m, 4H, CH₂). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ = 216.6 (d, ¹J_{RhC} = 43 Hz, Rh=C), 142.2 (CH⁴), 139.0 (CH¹), 131.6 (CH²), 118.5 (CH³), 99.5, 99.4 (d, ¹J_{RhC} = 5 Hz, =CH), 71.4, 66.0 (d, ¹J_{RhC} = 15 Hz, =CH), 52.9 (N-Me), 33.4, 32.3, 29.0, 28.4 (CH₂).

Anal. Calcd for C₁₄H₁₉ClNRh: C, 49.50; H, 5.64; N, 4.12. Found: C, 49.8; H, 6.0; N, 4.0.

Synthesis of complex **3a**.

A suspension of 40 mg (0.29 mmol) of N-methyl-2-carboxypyridine and 98 mg (0.15 mmol) of [IrCl(cod)]₂ in 2 mL of dry THF is heated at 65 °C for 2 hours under inert atmosphere. The resulting dark red solution is filtered *via* cannula and mixed with 5 mL of pentane, yielding a yellow precipitate that is further washed with 2 mL of pentane. The solid is dried *in vacuo* to yield 105 mg of **2b** (0.24 mmol, 84% yield).

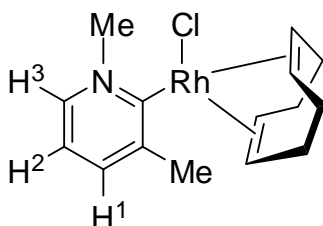


^1H NMR (500 MHz, CDCl_3): δ = 8.01 (d, 1H, $^3J_{\text{HH}} = 8.4$ Hz, H^4), 7.98 (d, 1H, $^3J_{\text{HH}} = 7.3$ Hz, H^1), 7.37 (dd, 1H, $^3J_{\text{HH}} = 8.4$ and 7.3 Hz, H^2), 6.90 (dd, 1H, $^3J_{\text{HH}} = 8.4$ and 7.3 Hz, H^3), 4.63 (m, 1H, $=\text{CH}_{\text{cod}}$), 4.59 (m, 1H, $=\text{CH}_{\text{cod}}$), 4.58 (s, 3H, N-Me), 2.88 (m, 1H, $=\text{CH}_{\text{cod}}$), 2.78 (m, 1H, $=\text{CH}_{\text{cod}}$), 3.32 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 1.86 (m, 1H, CH_2), 1.76-1.67 (m, 3H, CH_2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125 MHz, CDCl_3): δ = 210.4 (Ir=C), 142.5 (CH^4), 139.4 (CH^1), 133.3 (CH^2), 118.1 (CH^3), 85.1, 84.9 ($=\text{CH}$), 55.9 ($=\text{CH}$), 52.4 (N-Me), 50.3 ($=\text{CH}$), 34.0, 33.2, 29.5, 29.4 (CH_2).

Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{ClIrN}$: C, 39.20; H, 4.46; N, 3.27. Found: C, 39.4; H, 4.4; N, 3.4.

Synthesis of 2b

A suspension of 40 mg (0.26 mmol) of 1,3-dimethyl-2-carboxypyridine and 65 mg (0.13 mmol) of $[\text{RhCl}(\text{cod})]_2$ in 2 mL of dry THF is heated to 65° C for 2 hours. The solvent is removed *in vacuo* and the crude solid is extracted with toluene (2x2 mL). 5 mL of dry pentane are then added, the solution is filtered and the solvent removed *in vacuo* to yield a dark yellow solid. This product is further purified by crystallization from CH_2Cl_2 /pentane, resulting in 59 mg of **3a** (65% yield).



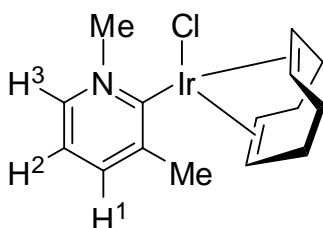
^1H NMR (500 MHz, CDCl_3): δ = 7.86 (d, 1H, $^3J_{\text{HH}} = 6.4$ Hz, H^3), 7.16 (d, 1H, $^3J_{\text{HH}} = 7.3$ Hz, H^1), 6.85 (dd, 1H, $^3J_{\text{HH}} = 6.4$ and 7.3 Hz, H^2), 5.01 (m, 1H, $=\text{CH}_{\text{cod}}$), 4.97 (m, 1H, $=\text{CH}_{\text{cod}}$), 4.88 (s, 3H, N-Me), 3.12 (s, 3H, C-Me), 3.05 (m, 2H, $=\text{CH}_{\text{cod}}$), 2.54-2.39 (m, 3H, CH_2), 2.32 (m, 1H, CH_2), 2.06-1.85 (m, 4H, CH_2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125 MHz, CDCl_3): δ = 218.2 (d, $^1J_{\text{RhC}} = 43$ Hz, $\text{Rh}=\text{C}$), 147.7 ($\underline{\text{C}}_{\text{q}}\text{-Me}$), 139.1 (CH^3), 131.6 (CH^1), 118.8 (CH^2), 98.6, 98.3 (d, $^1J_{\text{RhC}} = 6$ Hz, $=\text{CH}$), 68.6, 67.8 (d, $^1J_{\text{RhC}} = 13$ Hz, $=\text{CH}$), 52.3 (N-Me), 33.2, 32.0, 29.1, 28.4 (CH_2), 24.7 (Me).

Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{ClIrN}$: C, 50.94; H, 5.98; N, 3.96. Found: C, 50.7; H, 5.7; N, 3.5.

Synthesis of 3b

A suspension of 40 mg (0.26 mmol) of N-methyl-2-carboxypyridine and 89 mg (0.13 mmol) of $[\text{IrCl}(\text{cod})]_2$ in 2 mL of dry THF is heated to 65°C for 2 hours under inert atmosphere. The dark red solution is evaporated and the crude solid extracted with

toluene (3x 2mL). 5 mL of dry pentane are added to the toluene, the solution filtered and the solvent removed *in vacuo*, to yield a dark yellow solid which is crystallized from CH₂Cl₂/pentane mixtures (1:1) to yield 84 mg of **3b** (73 % yield).

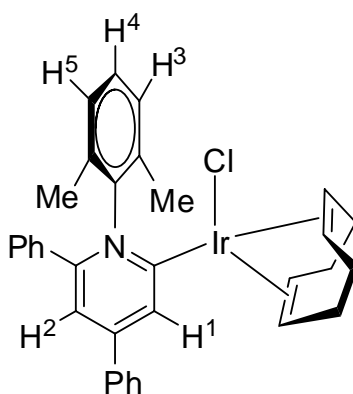


¹H NMR (500 MHz, CDCl₃): δ = 8.87 (d, 1H, ³J_{HH} = 6.4 Hz, H³), 7.28 (d, 1H, ³J_{HH} = 7.4 Hz, H¹), 6.85 (dd, 1H, ³J_{HH} = 6.4 and 7.4 Hz, H²), 4.64 (s, 3H, N-Me), 4.62 (m, 1H, =CH_{cod}), 4.54 (m, 1H, =CH_{cod}), 2.95 (s, 3H, C-Me), 2.71 (m, 2H, =CH_{cod}), 2.37-2.14 (m, 4H, CH₂), 1.83 (m, 1H, CH₂), 1.74-1.62 (m, 2H, CH₂), 1.58, (m, 1H, CH₂).
¹³C{¹H} NMR (125 , MHz, CDCl₃): δ = 211.0 (Ir=C), 148.1 (C_q-Me), 139.4 (CH³), 133.6 (CH¹), 118.4 (CH²), 83.7, 83.3, 52.7, 51.8 (=CH), 51.7 (N-Me), 33.8, 32.6, 29.7, 29.1 (CH₂), 24.4 (Me).

Anal. Calcd for C₁₅H₂₁ClIrN: C, 40.67; H, 4.78; N, 3.16. Found: C, 41.0; H, 5.1; N, 3.5.

Synthesis of **3c**.

A solution of 40 mg (0.11 mmol) of 1-*m*-xylyl-4,6-diphenyl-2-carboxypyridine and 35 mg (0.05 mmol) of [IrCl(cod)]₂ in 2 mL of dry THF is heated to 65°C for 2 hours under inert atmosphere. Solvent is removed *in vacuo* and the crude solid is crystallized from a toluene/pentane mixture (1:1) to yield 40 mg of a dark yellow solid, **3c** (54% yield).



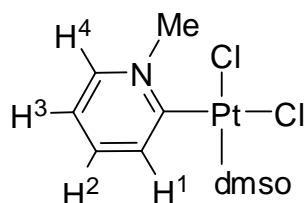
¹H NMR (500 MHz, CDCl₃): δ = 8.53 (d, 1H, ⁴J_{HH} = 2.3, H¹), 7.82 (m, 2H, Ph), 7.51 (m, 3H, Ph), 7.28 (m, 1H, Ph), 7.22 (m, 4H, Ph), 7.19 (d, 1H, ⁴J_{HH} = 2.3, H²), 7.17 (m, 2H, H⁴ and H⁵), 6.84 (m, 1H, H³), 4.55 (m, 1H, =CH_{cod}), 4.29 (m, 1H, =CH_{cod}), 3.45 (m, 1H, =CH_{cod}), 2.59 (s, 3H, Me), 2.39 (m, 1H, CH₂), 2.26 (m, 1H, =CH_{cod}), 2.10-1.91 (m, 2H, CH₂), 1.82-1.72 (m, 2H, CH₂) 1.69 (s, 3H, Me), 1.29-1.19 (m, 2H, CH₂), 1.00 (m,

1H, CH₂). ¹³C{¹H} NMR (125, MHz, CDCl₃): δ = 213.0 (Ir=C), 154.9 (C_{q-Ph-N}), 144.5 (C_q), 144.3 (C_{q-Xyl-N}), 136.5 (C_q), 136.3 (C_{q-Xyl}), 135.7 (CH¹), 134.9 (C_q), 132.9 (C_{q-Xyl}), 130.1, 129.4, 129.1 (CH_{Ph}), 129.0, 128.9 (CH⁴, CH⁵), 128.4, 127.9, 127.7 (CH_{Ph}), 127.2 (CH³), 119.7 (CH²) 84.6, 81.4, 56.3, 48.8 (=CH_{cod}), 36.5, 31.5, 30.7, 26.4 (CH₂), 21.5 (Me), 18.8 (Me).

Anal. Calcd for C₃₃H₃₃IrClN: C, 59.04; H, 4.95; N, 2.09; Found: C, 59.4; H, 4.9; N, 1.8.

Synthesis of 4a.

A suspension of 40 mg (0.29 mmol) of N-methyl-2-carboxypyridine and 109 mg (0.29 mmol) of [PtCl₂(dmsO)₂] in 2 mL of dry THF is heated at 70°C for 2 hours under inert atmosphere. Solvent is removed *in vacuo* and the resulting solid washed with methanol (2x2 mL) to yield 93 mg of **4a** (60 % yield) as an off-white product.

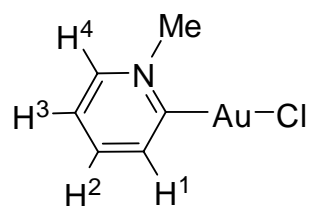


¹H NMR (500 MHz, CDCl₃): δ = 8.67 (d, 1H, ³J_{HH} = 6.2 Hz, H⁴), 8.12 (d, 1H, ³J_{HH} = 7.3 Hz, ³J_{HPt} ~ 35 Hz, H¹), 7.78 (dd, 1H, ³J_{HH} = 6.2, 7.3 Hz, H²), 7.44 (dd, 1H, ³J_{HH} = 6.2, 7.3 Hz, H³), 4.54 (s, 3H, Me), 2.54 (s, 6H, dissociated dmsO). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 164.9 (Pt=C), 144.1 (CH⁴), 138.2 (CH²), 138.0 (CH¹), 121.4 (CH³), 52.0 (N-Me), 40.5 (dissociated dmsO).

Anal. Calcd for C₈H₁₃Cl₂NOPtS: C, 21.98; H, 3.00; N, 3.20. Found: C, 22.1; H, 2.7; N, 3.3.

Synthesis of 5a

A suspension of 30 mg (0.22 mmol) of N-methyl-2-carboxypyridine and 64 mg (0.22 mmol) of [AuCl(SMe₂)] in 2 mL of dry THF is heated at 70°C for 1.5 hours under inert atmosphere. Solvent is removed *in vacuo* and the resulting solid is extracted with dry CH₂Cl₂ (5 mL). A yellow solid precipitates upon addition of 10 mL of pentane. The solution is filtered off and the yellow solid dried *in vacuo* to yield 43 mg of **4a** (59 % yield).

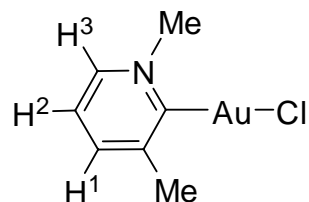


¹H NMR (500 MHz, CDCl₃): δ = 8.26 (d, 1H, ³J_{HH} = 6.4 Hz, H⁴), 7.98 (d, 1H, ³J_{HH} = 8.2 Hz, H¹), 7.80 (dd, 1H, ³J_{HH} = 8.2 and 7.8 Hz, H²), 7.40 (dd, 1H, ³J_{HH} = 6.4 and 7.8 Hz, H³), 4.46 (s, 3H, Me). **¹³C{¹H} NMR** (125 , MHz, CDCl₃): δ = 187.6 (Au=C), 142.2 (CH⁴), 140.3 (CH¹), 137.8 (CH²), 121.9 (CH³), 54.7 (N-Me).

Anal. Calcd for C₆H₇AuClN: C, 22.14; H, 2.17; N, 4.30. Found: C, 22.5; H, 2.3; N, 4.2.

Synthesis of 5b.

A suspension of 40 mg (0.26 mmol) of 1,3-dimethyl-2-carboxypyridine and 76 mg (0.26 mmol) of [AuCl(SMe₂)] in 2 mL of dry THF is heated to 70°C for 1.5 hours under inert atmosphere. Solvent is removed *in vacuo* and the resulting solid is extracted with dry CH₂Cl₂ (5 mL). A white solid precipitates upon addition of 10 mL of pentane. The solution is filtered off and the white solid dried *in vacuo* to yield 62 mg of **5b** (70 % yield).

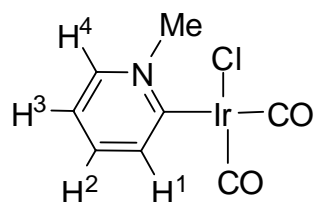


¹H NMR (500 MHz, CDCl₃): δ = 8.18 (d, 1H, ³J_{HH} = 6.4 Hz, H³), 7.78 (d, 1H, ³J_{HH} = 7.8 Hz, H¹), 7.32 (dd, 1H, ³J_{HH} = 6.4 and 7.8 Hz, H²), 4.47 (s, 3H, N-Me), 2.69 (s, 3H, Me). **¹³C{¹H} NMR** (125 , MHz, CDCl₃): δ = 188.7(Au=C), 148.1 (C_q), 139.4 (CH³), 137.1 (CH¹), 121.5 (CH²), 54.2 (N-Me), 25.2 (Me).

Anal. Calcd for C₇H₉AuClN: C, 24.76; H, 2.67; N, 4.12. Found: C, 24.7; H, 2.6; N, 4.1.

Synthesis of 6a.

CO is bubbled through a solution of **3a** (20 mg; 0.047 mmol) in 2 mL of CH₂Cl₂. The color changes from orange to yellow. Solvent is removed *in vacuo* and the resulting solid is washed with pentane (3x2mL) to produce **6a** quantitatively.

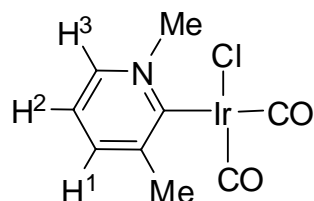


IR (nujol): $\nu(\text{CO})$ 2062, 1980 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 8.21 (d, 1H, $^3J_{\text{HH}} = 6.2$ Hz, H^4), 8.14 (d, 1H, $^3J_{\text{HH}} = 8.0$ Hz, H^1), 7.74 (t, 1H, $^3J_{\text{HH}} = 7.7$ Hz, H^2), 7.32 (dd, 1H, $^3J_{\text{HH}} = 6.2, 8.0$ Hz, H^3), 4.54 (s, 3H, Me). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125 MHz, CDCl_3): δ = 197.4 (Ir=C), 181.8 (CO), 169.5 (CO), 143.0 (CH^4), 140.3 (CH^1), 136.4 (CH^2), 121.5 (CH^3), 53.8 (N-Me), 28.0 (Me).
Anal. Calcd for $\text{C}_8\text{H}_7\text{ClIrNO}_2$: C, 25.50; H, 1.87; N, 3.72. Found: C, 25.2; H, 2.1; N, 3.4.

Synthesis of 6b.

This complex is prepared similarly, using 20 mg (0.045 mmol) of **3b** dissolved in 2 mL of CH_2Cl_2 .



IR (nujol): $\nu(\text{CO})$ 2060, 1977 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ = 8.08 (d, 1H, $^3J_{\text{HH}} = 5.9$ Hz, H^3), 7.63 (d, 1H, $^3J_{\text{HH}} = 7.8$ Hz, H^1), 7.25 (dd, 1H, $^3J_{\text{HH}} = 5.9$ and 7.8 Hz, H^2), 4.55 (s, 3H, N-Me), 2.83 (s, 3H, C-Me). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125 MHz, CDCl_3): δ = 197.4 (Ir=C), 182.3, 169.0 (Ir-CO), 149.3 (C_q), 140.4 (CH^3), 137.2 (CH^1), 121.6 (CH^2), 53.6 (N-Me), 25.3 (Me).

HRMS (EI) Calcd for $\text{C}_9\text{H}_9\text{NO}_2\text{ClIr}$ requires 390.9951, Found 390.9968.

X-ray structural determination for complexes 3b and 5b:

The most relevant crystal and refinement data are collected in Tables S.1 and S.2. In both cases, crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into saturated solutions of the complexes in dichloromethane. Diffraction data were recorded on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Images were collected on a 65 mm fixed crystal-detector distance, using the oscillation method, with 1st oscillation and

(1.5 – 2) s variable exposure time per image. Data collection strategy was calculated with the program CrysAlis Pro CCD.⁷ Data reduction and cell refinement was performed with the program CrysAlis Pro RED.⁷ An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.⁷ In all cases the software package WINGX⁸ was used for space group determination, structure solution and refinement. The structure for the complex **3b** was solved by direct methods using SIR2004⁹ and **5b** by Patterson interpretation and phase expansion using DIRDIF.¹⁰ Isotropic least-squares refinement on F^2 using SHELXL97¹¹ was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and their coordinates were refined riding on their parent atoms. The function minimized was $([\sum w F_o^2 - F_c^2]/\sum w(F_o^2))^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (for **3b**, $a = 0.0389$, $b = 3.9074$ and for **5b**, $a = 0.0777$, $b = 3.5800$) with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography International.¹² Geometrical calculations were made with PARST.¹³

⁷ CrysAlis^{Pro} CCD, CrysAlis^{Pro} RED. Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK. (2008).

⁸ L.J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

⁹ M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2005, **38**, 381.

¹⁰ P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, *The DIRDIF Program System*, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.

¹¹ G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

¹² *Tables for X-Ray Crystallography*; Kynoch Press, Birmingham, U.K., (1974); Vol. IV (present distributor: Kluwer Academic Publishers; Dordrecht, The Netherlands).

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3. Table S.1. Crystal data and structure refinement for **3b**.

Identification code	mrm142b	
Empirical formula	C15 H21 Cl Ir N	
Formula weight	442.98	
Temperature	293(2) K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.2207(2) Å	$\alpha = 90^\circ$.
	b = 11.3062(1) Å	$\beta = 110.736(2)^\circ$.
	c = 13.6376(2) Å	$\gamma = 90^\circ$.
Volume	1473.84(4) Å ³	
Z	4	
Density (calculated)	1.996 Mg/m ³	
Absorption coefficient	19.046 mm ⁻¹	
F(000)	848	
Crystal size	0.037 x 0.098 x 0.137 mm ³	
Theta range for data collection	4.63 to 74.36°.	
Index ranges	-12<=h<=11, -14<=k<=10, -16<=l<=15	
Reflections collected	6182	
Independent reflections	2913 [R(int) = 0.0219]	
Completeness to theta = 74.36°	97.2 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2913 / 0 / 165	
Goodness-of-fit on F ²	1.142	
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0696	
R indices (all data)	R1 = 0.0332, wR2 = 0.0831	
Largest diff. peak and hole	0.711 and -1.289 e.Å ⁻³	

4. Table S.2. Crystal data and structure refinement for **5b**.

Identification code	mrm173sp	
Empirical formula	C7 H9 Au Cl N	
Formula weight	339.57	
Temperature	100(2) K	
Wavelength	1.5418 Å	
Crystal system	orthorhombic	
Space group	P bca	
Unit cell dimensions	a = 7.1822(2) Å	$\alpha = 90^\circ$.
	b = 14.0369(3) Å	$\beta = 90^\circ$.
	c = 16.6733(3) Å	$\gamma = 90^\circ$.
Volume	1680.93(7) Å ³	
Z	8	
Density (calculated)	2.684 Mg/m ³	
Absorption coefficient	35.194 mm ⁻¹	
F(000)	1232	
Crystal size	0.093 x 0.046 x 0.019 mm ³	
Theta range for data collection	5.31 to 73.89°.	
Index ranges	-6<=h<=8, -17<=k<=17, -20<=l<=20	
Reflections collected	8548	
Independent reflections	1698 [R(int) = 0.0556]	
Completeness to theta = 73.89°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1698 / 0 / 93	
Goodness-of-fit on F ²	1.116	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1090	
R indices (all data)	R1 = 0.0444, wR2 = 0.1130	
Largest diff. peak and hole	2.455 and -1.837 e.Å ⁻³	