Supporting Information for:

‘Highly active iridium(I) complexes for the selective hydrogenation of carbon-carbon multiple bonds’

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General Experimental Details:

Dichloromethane was dried by heating to reflux over calcium hydride then distilled under nitrogen.

1-Methylcyclohex-1-ene and 2,3-dimethylbut-2-ene were filtered through a plug of alumina, and distilled from KOH prior to use.

Gas Chromatography/Mass Spectrometry analysis was performed using a Hewlett Packard 6890 gas chromatograph (GC) coupled to a 5973 mass selective detector. A DB-1MS J&W column (25 m length, 0.2 mm inner diameter, 0.33 μm film thickness) was used with helium carrier gas. Mass spectra were obtained in electron impact ionisation (EI) mode. The helium carrier gas was set to constant flow at 1 ml/min. The inlet temperature was set to 200°C and the detector temperature set to 250 °C. The GC oven held 50°C for 5 min, then increased at a rate of 10°C/min for 1 min. Injections were split at a ratio of 50:1 and the injection volume was 1 μl. Octane was used as an internal standard.

General Procedure for Synthesis of Complexes ***1a-c***:

A flame dried and nitrogen cooled Schlenk tube was charged with η^4-cycloocta-1,5-dieneiridium(I) chloride dimer and dry benzene (10 mL). The solution was treated with freshly prepared 1M sodium ethoxide solution and stirred for 10 minutes. After this time, 1,3-dimesitylimidazolium chloride was added and the mixture stirred for 5 h at r.t. The solvent was removed under high vacuum and the residue triturated with dry ether prior to filtration through celite under N_2. After solvent exchange to dry THF (15 mL), $AgPF_6$ was added and the resultant slurry stirred for 30 minutes at r.t. After filtration through celite under N_2, the solution was treated with phosphine and the resultant ruby red solution was stirred for 2 h. Purification by recrystallisation from DCM/Et_2O yielded the desired complex.

Following the general procedure, data are reported as: (a) amount of η^4-cycloocta-1,5-dieneiridium(I) chloride dimer, (b) volume of sodium ethoxide, (c) amount of imidazolium salt, (d) amount of $AgPF_6$, (e) amount of phosphine, and (f) product yield.

Complex ***1a***:

(a) 0.2 g, 0.298 mmol, (b) 0.6 mL, 0.595 mmol, (c) 0.203 g, 0.595 mmol, (d) 0.150 g, 0.595 mmol, (e) tribenzylphosphine, 0.181 g, 0.595 mmol, and (f) 0.373 g, 59%. (Found: C, 56.7; H, 5.3; N, 2.7. Calc. for $C_{50}H_{57}F_6IrN_2P_2$: C, 57.0; H, 5.45; N, 2.7%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3045, 2989, 2303, 1603 and 1495; δ_H(400 MHz; [D_6]acetone): 7.79 (2 H, s, olefinic C*H*), 7.40 (2 H, s, Ar*H*), 7.34 (2 H, s, Ar*H*), 7.30-7.26 (9 H, m, Ar*H*), 6.98-6.96 (6 H, m, Ar*H*), 4.72-4.70 (2 H, m, COD C*H*), 3.43-3.38 (2 H, m, COD C*H*), 3.02 (6 H, d, $^2J_{PH}$ 8.8, PCH_2Ar), 2.57 (6 H, s, $ArCH_3$), 2.51 (6 H, s, $ArCH_3$), 2.47 (6 H, s, $ArCH_3$), 1.80-1.77 (2 H, m, COD CH_2), 1.58-1.49 (4 H, m, COD CH_2) and 1.37-1.31 (2 H, m, COD CH_2); δ_C(100 MHz; [D_6]acetone): 176.5, 141.1, 137.4, 137.0, 136.2, 134.3, 134.3, 131.0, 130.9, 130.7, 129.5, 127.9, 127.7, 87.2, 75.8, 32.3, 31.0, 30.7, 21.1, 20.6 and 19.9; δ_P(162 MHz; [D_6]acetone): -6.3 (*P*Bn_3) and -143.5 (*P*F_6); m/z (ESI) 907.3852 (Calc. for $C_{50}H_{57}{}^{191}IrN_2P$ [M-PF_6]$^+$: 907.3860).

Complex ***1b***:

(a) 0.2 g, 0.298 mmol, (b) 0.6 mL, 0.595 mmol, (c) 0.203 g, 0.595 mmol, (d) 0.150 g, 0.595 mmol, (e) triphenylphosphine, 0.156 g, 0.595 mmol, and (f) 0.375 g, 62%. $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3050, 2981, 2305, 1608 and 1480; δ_H(400 MHz; $CDCl_3$): 7.47-7.41 (5 H, m, C*H*), 7.33-7.28 (6 H, m, C*H*), 7.15-7.08 (6 H, m, C*H*), 6.99 (2 H, s, C*H*), 6.65 (2 H, s, C*H*), 4.41-4.33 (2 H, m, C*H*), 3.38-3.25 (2 H, m, C*H*), 2.36 (6 H, s, CH_3), 2.12 (6 H, s, CH_3), 1.77 (6 H, s, CH_3), 1.71-1.50 (6 H, m, CH_2) and 1.29-1.25 (2 H, m, CH_2); δ_C(100 MHz; $CDCl_3$): 177.0, 139.9, 136.0, 135.9, 135.4, 135.0, 131.5, 131.0, 130.5, 129.9, 128.8, 127.1, 80.7, 80.6, 78.1, 32.1, 30.4, 21.4, 21.1 and 19.2; δ_P(162 MHz; $CDCl_3$): 17.1 (*P*Ph_3) and -143.5 (*P*F_6); m/z (ESI) 867.3407 (Calc. for $C_{47}H_{51}{}^{193}IrN_2P$ [M-PF_6]$^+$: 867.3414).

*Complex **1c***:

(a) 0.2 g, 0.298 mmol, (b) 0.6 mL, 0.595 mmol, (c) 0.203 g, 0.595 mmol, (d) 0.150 g, 0.595 mmol, (e) dimethylphenylphosphine, 0.085 mL, 0.595 mmol, and (f) 0.371 g, 71%.

(Found: C, 50.0; H, 5.3; N, 3.0. Calc. for $C_{37}H_{47}F_6IrN_2P_2$: C, 50.05; H, 5.3; N, 3.15%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3045, 2985, 2302, 1606 and 1484; δ_H(400 MHz; $CDCl_3$): 7.41-7.36 (4 H, m, Ar*H*), 7.30-7.28 (3 H, m, Ar*H* and olefinic C*H*), 7.06 (2 H, s, Ar*H*), 6.92 (2 H, s, Ar*H*), 4.30-4.28 (2 H, m, COD C*H*), 3.48-3.45 (2 H, m, COD C*H*), 2.39 (6 H, s, ArCH_3), 2.21 (6 H, s, ArCH_3), 2.15, (6 H, s, ArCH_3), 1.78-1.56 (8 H, m, COD CH_2) and 1.50 (6 H, d, $^2J_{PH}$ 8.4, CH_3); δ_C(100 MHz; $CDCl_3$): 177.3, 140.1, 135.7, 134.8, 132.0, 130.9, 130.2, 129.9, 128.9, 126.0, 83.5, 83.3, 77.4, 76.1, 31.6, 30.6, 21.1, 20.4, 19.3, 16.6 and 16.3; δ_P(162 MHz; $CDCl_3$): -13.3 (*P*Me_2Ph) and -143.5 (*P*F_6); m/z (ESI) 743.3107 (Calc. for $C_{37}H_{47}{}^{193}IrN_2P$ $[M-PF_6]^+$: 743.3101).

Standard Hydrogenation Procedure:

A flame dried and nitrogen cooled 25 mL round bottomed flask was charged with the iridium complex and dry DCM (4 mL), followed by the substrate (0.2 mmol). The reaction vessel was cooled to -78°C in a dry ice/acetone bath, prior to being evacuated and filled with hydrogen gas three times *via* a balloon. The reaction mixture was then allowed to warm to room temperature and stirred vigorously for the allotted reaction time before removal of the hydrogen atmosphere. The reaction mixture was concentrated under reduced pressure and the catalyst residues were removed by trituration with diethyl ether (~10 mL) and removed by filtration through a plug of silica. Concentration of the filtrate under reduced pressure yielded the product/substrate mixtures, which were analysed without further purification.

Hydrogenation of Volatile Olefins

A flame dried and nitrogen cooled 25 mL 1-neck round bottomed flask was charged with the iridium complex and dry dichloromethane with 2.5% (v/v) octane (4 ml), followed by addition of the substrate (0.2 mmol). The reaction vessel was cooled to -78°C in a dry ice/acetone bath, prior to being evacuated and filled with hydrogen gas three times *via* a balloon. The reaction mixture was then allowed to warm to room temperature and stirred vigorously for the allotted reaction time. The hydrogen atmosphere was removed from the system and the reaction mixture was analysed directly by GC/MS.

Selective Hydrogenation Using Benzamide as Poison:

A flame dried and nitrogen cooled 25 mL round bottomed flask was charged with the substrate (186 mg, 1 mmol) and dry DCM (10 mL), followed by the iridium complex (1 mg, 0.001 mmol) and benzamide (18.2 mg, 0.15 mmol). The reaction vessel was cooled to -78 ºC in a dry ice/acetone bath, prior to being evacuated and filled with hydrogen gas three times *via* a balloon. The reaction mixture was then allowed to warm to room temperature and stirred vigorously for the allotted reaction time before removal of the hydrogen atmosphere. The reaction mixture was concentrated under reduced pressure and the residue was triturated with diethyl ether. The diethyl ether solution was washed three times with 2M hydrochloric acid, filtered through a plug of silica to remove the catalyst residues, and concentrated under reduced pressure to yield the product, which was analysed without further purification.

Spectral details for hydrogenation products:

3-(6-Bromo-3-methoxy-2-methylphenyl)-N-*methoxy*-N-*methylpropanamide,* ***3***:

$\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3049, 3005, 2965, 2940, 2839, 1658 and 1573; δ_H(400 MHz; $CDCl_3$): 7.35 (1 H, d, *J* 8.7, ArC*H*), 6.62 (1 H, d, *J* 8.8, ArC*H*), 3.80 (3 H, s, ArOC*H₃*), 3.66 (3 H, s, NOC*H₃*), 3.21 (3 H, s, NC*H₃*), 3.15-3.11 (2H, m, CH_2CH_2), 2.64-2.60 (2 H, m, CH_2CH_2) and 2.25 (3 H, s, ArC*H₃*); δ_C(100 MHz; $CDCl_3$): 172.5, 156.1, 138.5, 129.3, 126.0, 114.9, 109.0, 60.3, 54.7, 31.2, 29.9, 27.5 and 11.3; *m/z* (EI) 316.0541 (Calc. for $C_{13}H_{19}BrNO_3$ $[M + H]^+$: 316.0543).

1-Bromo-4-ethylbenzene, ***5***:[1]

$\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2970, 2935, 2876 and 1489; δ_H(400 MHz; $CDCl_3$): 7.41 (2 H, d, *J* 8.4, ArC*H*), 7.09 (2 H, d, *J* 8.5, ArC*H*), 2.62 (2 H, q, *J* 7.6, $ArCH_2CH_3$) and 1.24 (3 H, t, *J* 7.6, CH_2CH_3); δ_C(100 MHz; $CDCl_3$): 143.2, 131.3, 129.7, 119.3, 28.3 and 15.5.

4-Phenylbutan-2-one, 7:[2]

$\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3065, 3030, 2930 and 1716; δ_H(400 MHz; $CDCl_3$): 7.32-7.27 (2 H, m, ArC*H*), 7.23-7.19 (3 H, m, ArC*H*), 2.93-2.89 (2 H, m, CH_2CH_2), 2.79-2.76 (2 H, m, CH_2CH_2) and 2.15 (3 H, s, $COCH_3$); δ_C(100 MHz; $CDCl_3$): 207.9, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1 and 29.8.

*Ethyl 3-(4-bromophenyl)propanoate, **9***:[3]

ν_{max}(CH_2Cl_2)/cm^{-1} 2983, 2938, 2873 and 1730; δ_H(400 MHz; $CDCl_3$): 7.40 (2 H, d, *J* 8.4, Ar*CH*), 7.08 (2 H, d, *J* 8.4, Ar*CH*), 4.13 (2 H, q, *J* 7.2, $COCH_2CH_3$), 2.91 (2 H, t, *J* 7.6, CH_2CH_2), 2.60 (2 H, t, *J* 7.5, CH_2CH_2) and 1.23 (3 H, t, *J* 7.2, CH_2CH_3); δ_C(100 MHz; $CDCl_3$): 172.6, 139.6, 131.5, 130.1, 120.0, 60.5, 35.7, 30.3 and 14.2.

*Ethyl 3-(4-(benzyloxy)phenyl)propanoate, **11***:[4]

ν_{max}(CH_2Cl_2)/cm^{-1} 3067, 3035, 2983, 2935, 2873 and 1728; δ_H(400 MHz; $CDCl_3$): 7.46-7.32 (5 H, m, Ar*CH*), 7.14 (2 H, d, *J* 8.7, Ar*CH*), 6.93 (2 H, d, *J* 8.7, Ar*CH*), 5.06 (2 H, s, $PhCH_2O$), 4.15 (2 H, q, *J* 7.2, $COCH_2CH_3$), 2.92 (2 H, t, *J* 7.5, CH_2CH_2), 2.61 (2 H, t, *J* 7.4, CH_2CH_2) and 1.26 (3 H, t, *J* 7.2, CH_2CH_3); δ_C(100 MHz; $CDCl_3$): 171.9, 156.3, 136.1, 131.9, 128.2, 127.5, 126.9, 126.4, 113.8, 69.0, 59.3, 35.2, 29.1 and 13.2.

*Ethyl 3-(4-nitrophenyl)propanoate, **13***:[5]

ν_{max}(CH_2Cl_2)/cm^{-1} 3061, 2984, 2941, 2874, 1731, 1606, 1522, 1348 and 1190; δ_H(400 MHz; $CDCl_3$): 8.14 (2 H, d, *J* 8.8, Ar*CH*), 7.37 (2 H, d, *J* 8.8, Ar*CH*), 4.12 (2 H, q, *J* 7.2, $COCH_2CH_3$), 3.05 (2 H, t, *J* 7.5, CH_2CH_2), 2.66 (2 H, t, *J* 7.5, CH_2CH_2) and 1.22 (3 H, t, *J* 7.2, CH_2CH_3); δ_C(100 MHz; $CDCl_3$): 172.1, 148.3, 146.7, 129.2, 123.7, 60.7, 35.0, 30.7 and 14.2.

*Ethyl 3-(3-iodophenyl)propanoate, **15***:

ν_{max}(CH_2Cl_2)/cm^{-1} 3065, 2983 and 1730; δ_H(400 MHz; $CDCl_3$): 7.58-7.53 (2 H, m, Ar*CH*), 7.17 (1 H, d, *J* 7.8, Ar*CH*), 7.02 (1 H, t, *J* 7.8, Ar*CH*), 4.13 (2 H, q, *J* 7.2, $COCH_2CH_3$), 2.89 (2 H, t, *J* 7.6, CH_2CH_2), 2.60 (2 H, t, *J* 7.5, CH_2CH_2) and 1.24 (3 H, t, *J* 7.2, CH_2CH_3); δ_C(100 MHz; $CDCl_3$): 171.5, 142.0, 136.4, 134.3, 129.2, 126.6, 93.4, 59.5, 34.6, 29.4 and 13.2; *m*/*z* (EI) 322.0302 (Calc. for $C_{11}H_{17}INO_2$ $[M + NH_4]^+$: 322.0298).

*Ethyl 3-(2-iodophenyl)propanoate, **17***:[6]

ν_{max}(CH_2Cl_2)/cm^{-1} 3067, 2983 and 1730; δ_H(400 MHz; $CDCl_3$): 7.82 (1 H, dd, *J* 7.6 and 1.0, ArC*H*), 7.30-7.24 (2 H, m, ArC*H*), 6.92-6.88 (1 H, m, ArC*H*), 4.15 (2 H, q, *J* 7.1, COC*H*$_2$CH$_3$), 3.05 (2 H, t, *J* 7.9, C*H*$_2$CH$_2$), 2.62 (2 H, t, *J* 7.9, CH$_2$C*H*$_2$) and 1.25 (3 H, t, *J* 7.1, CH$_2$C*H*$_3$); δ_C(100 MHz; $CDCl_3$): 171.4, 142.1, 138.6, 128.5, 127.4, 127.1, 99.3, 59.5, 34.9, 33.4 and 13.2.

*Methylcyclohexane, **19***:

R_t (parent olefin, **18**) = 4.61 min.

R_t (**19**) = 3.56 min.

R_t (octane) = 5.75 min.

*2,3-Dimethylbutane, **21***:

R_t (parent olefin, **20**) = 2.28 min.

R_t (**21**) = 1.82 min.

R_t (octane) = 5.72 min.

*4-Pentyl-1-propylbenzene, **23***:[7]

ν_{max}($CDCl_3$)/cm^{-1} 3662, 3366, 3131, 3034, 2855, 2246, 1792, 1682, 1609 and 1574; δ_H(400 MHz; $CDCl_3$): 7.11 (4 H, s, ArC*H*), 2.60-2.56 (4 H, m, C*H*$_2$), 1.68-1.60 (4 H, m, C*H*$_2$), 1.37-1.33 (4 H, m, C*H*$_2$), 0.98 (3 H, t, *J* 7.3, C*H*$_3$) and 0.93 (3 H, t, *J* 3.8, C*H*$_3$); δ_C(100 MHz; $CDCl_3$): 140.4, 140.1, 128.8, 128.7, 38.3, 36.2, 32.2, 31.9, 25.2, 23.2, 14.5 and 14.3; *m/z* (EI) 190.1719 (Calc. for $C_{14}H_{22}$ [M]$^+$: 190.1716).

*(Z)-4-Pentyl-1-(prop-1-enyl)benzene, **24***:

ν_{max}($CDCl_3$)/cm^{-1} 3036, 3030, 3026, 3016, 3013, 2960, 2932, 2859, 2254 and 1512; δ_H(400 MHz; $CDCl_3$): 7.28 (2 H, d, *J* 8.1, ArC*H*), 7.19 (2 H, d, *J* 8.1, ArC*H*), 6.45 (1 H, dd, *J* 11.6 and 1.6, C*H*=CH), 5.79 (1 H, dq, *J* 11.6 and 7.2, CH=C*H*), 2.64 (2 H, t, *J* 7.7, ArC*H*$_2$), 1.94 (3 H, dd, *J* 7.2 and 1.8, CHC*H*$_3$), 1.72-1.63 (2 H, m, C*H*$_2$), 1.42-1.32 (4 H, m, C*H*$_2$) and 0.93 (3 H, t, *J* 6.4, CH$_2$C*H*$_3$); δ_C(100 MHz; $CDCl_3$): 141.3, 135.2, 130.1, 129.0, 128.4, 126.0, 35.9, 31.8, 31.4, 22.8, 14.9 and 14.8.

(E)-4-Pentyl-1-(prop-1-enyl)benzene:

δ_H(400 MHz; $CDCl_3$): 7.27 (2 H, d, *J* 7.9, ArC*H*), 7.13 (2 H, d, *J* 7.9, ArC*H*), 6.40 (1 H, d, *J* 15.4, C*H*=CH), 6.22 (1 H, dq, *J* 15.7 and 6.5, CH=C*H*), 2.64 (2 H, t, *J* 7.7, ArCH_2), 1.90 (3 H, dd, *J* 6.6 and 1.5, CHCH_3), 1.72-1.63 (2 H, m, CH_2), 1.42-1.32 (4 H, m, CH_2) and 0.93 (3 H, t, *J* 6.4, CH_2CH_3).

NB: The *Z*- and *E*-olefins **24** were formed as an inseparable mixture.

References:

1 M. Yasuda, Y. Onishi, M. Ueba, T. Miyai and A. Baba, *J. Org. Chem.*, 2001, **66**, 7741.

2 T. Inagaki, L. T. Phong, A. Furuta, J.-I. Ito and H. Nishiyama, *Chem. Eur. J.*, 2010, **16**, 3090.

3 M. E. Sloan, A. Staubitz, K. Lee and I. Manners, *Eur. J. Org. Chem.*, 2011, 672.

4 S. N. Louis, T. L. Nero, D. Iakovidis, F. M. Colagrande, G. P. Jackman and W. J. Louis, *Eur. J. Med. Chem.*, 1999, **34**, 919.

5 C. Nájera and L. Botella, *Tetrahedron*, 2005, **61**, 9688.

6 J. Tummatorn and G. B. Dudley, *Org. Lett.*, 2011, **13**, 1572.

7 H. H. Wasserman and A. R. Doumaux, *J. Am. Chem. Soc.*, 1966, **88**, 4517.