Electronic Supplementary Information for '*A New Family of Metallaboratrane Complexes Based on 7-Azaindole: B-H Activation Mediated by Carbon Monoxide.*'

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Experimental

General considerations: All manipulations were performed in a Braun glovebox with an O_2 and H_2O atmosphere of below 5 ppm or by using standard Schlenk techniques. Ir(COD)Tai was prepared according to a published procedure.[S1] Solvents (toluene, THF, Et_2O) were dried using a Grubbs' alumina system, and were kept in Young's ampoules under N_2 over molecular sieves (4 Å). Dry n-pentane (<0.05 ppm H_2O) was purchased from Fluka and was kept in a Young's ampoule under N_2 over molecular sieves (4 Å). Deuterated toluene was degassed by three freeze-thaw cycles, dried by refluxing over Na for 12 hours, and kept in a Young's ampoule over 4 Å molecular sieves under N_2. ^{1}H-NMR, ^{11}B{^{1}H}-NMR, ^{11}B-NMR and DEPT-135 spectra were recorded on a JEOL ECP300 spectrometer operating at 300 MHz (^{1}H). ^{13}C{^{1}H}-NMR and correlation experiments spectra were recorded on a Varian VNMR S500 operating at 500 MHz (^{1}H). The spectra were referenced internally, to the residual protic solvent (^{1}H) or the signals of the solvent (^{13}C). ^{11}B{^{1}H}-NMR and ^{11}B-NMR spectra were referenced externally relative to $BF_3{\cdot}OEt_2$. Mass spectra were recorded on a VG Analytic Quattro in ESI$^+$ mode. Elemental analyses were performed at the microanalytical laboratory of the School of Chemistry at the University of Bristol. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer (solution, NaCl cell) or a Perkin-Elmer Spectrum 100 FTIR spectrometer (solid state, neat) from 4000 cm^{-1} to 650 cm^{-1}.

$Ir(CO)_2(C_8H_{13})\{\kappa^3$-*NNB*-B(azaindoyl)$_3$) (4)

25 mg of Ir(COD)Tai (0.038 mmol) were charged in a Young's NMR tube in the glovebox and dissolved in 0.5-0.6 mL of d^8-toluene to give a bright yellow solution. The NMR tube was removed from the glovebox and connected to a vacuum line (if the complex does not dissolve readily, gentle heating will promote solvation) and the inert atmosphere in the NMR tube removed by two freeze-thaw cycles. The solution was allowed to equilibrate at RT and the NMR tube was connected to a CO cylinder and pressurised to 1.5-1.6 bar and vigorously shaken under the dynamic positive pressure. After a few minutes the colour of the solution changes to pale yellow, then pale pink and finally almost colourless. The NMR tube was removed from the CO cylinder and spectroscopic data recorded. ^{1}H-NMR (300 MHz) $\delta(C_5D_5CD_3)$: 8.16 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 4.4 Hz, azaindole), 7.83 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 4.4 Hz), 7.76 (2H, m, azaindole), 7.72 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.41 (1H, d, $^3J_{HH}$= 3.7 Hz, azaindole), 7.15 (1H, $^3J_{HH}$ = 2.9 Hz, azaindole), 7.13 (2H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7.3 Hz azaindole), 6.81 (1H, m, azaindole), 6.62 (1H, d, $^3J_{HH}$ = 2.9 Hz, azaindole), 6.36 (2H, 2 overlapping d coinciding at the centre, $^3J_{HH}$ = 2.9 Hz, azaindole), 6.26 (2H, m, azaindole), 5.46 (2H, m, C*H*=C*H*), 2.21 (1H, broad, cyclo-octenyl), 1.86 (2H, m, cyclo-octenyl), 1.75 (2H, m, cyclo-octenyl), 1.60 (1H, m, cyclo-octenyl), 1.41 (1H, broad s, cyclo-octenyl), 1.15 (3H, m, cyclo-octenyl and Ir-C*H*), -0.07 (1H, broad s, C*H*H α-position to Ir-CH); ^{13}C{^{1}H}-NMR (125 MHz) $\delta(C_5D_5CD_3)$: 179.1, 170.0 (s, *C*O), 156.8, 156.5, 152.5, 142.7, 142.4, 142.2, 132.4, 131.1, 130.8, 130.4, 129.8, 128.9, 128.8, 127.4, 123.4, 121.7, 121.4, 115.5, 115.4, 115.3, 104.2, 103.5, 101.3 (azaindole and *C*H=*C*H), 46.2, 44.6, 31.6, 28.7, 25.7 (*C*H$_2$s of cyclo-octenyl), 17.0 (Ir-*C*H); ^{11}B{^{1}H}-NMR $\delta(C_5D_5CD_3)$: 5.83 (s, $\Delta\nu_{1/2}$ = 42.1 Hz); ^{11}B-NMR $\delta(C_5D_5CD_3)$: 5.83 (s); IR (toluene): 2059.8 cm^{-1}, 2009.2 cm^{-1} ν(CO); IR (THF): 2059.8 cm^{-1}, 2011.7 cm^{-1} ν(CO). The reaction sometimes adopts in the end a blue-green hue, but the only detectable species by ^{1}H, ^{11}B{^{1}H} and ^{11}B-NMR spectroscopy is the title compound. When samples were left for prolonged periods of time at RT (*ie* 12 hours - 2 days), a blue precipitate was formed. Nevertheless the only major species detected by NMR is **4**. The reaction has also been repeated in d^8-THF with the title compound being formed in 100% spectroscopic yield. Attempts to crystallise compound (**4**) in an atmosphere of CO were unsuccessful and resulted in the isolation of (**5**).

Ir(CO)(C_8H_{13}){κ^3-*NNB*-B(azaindoyl)$_3$) (5)

100 mg of Ir(COD)Tai (0.15 mmol) were charged in a Schlenk tube in the glovebox. They were dissolved in toluene (approx 12 mL) at RT by vigorous stirring to give a bright yellow solution. The Schlenk was then equipped with a septum and CO was bubbled through by means of a balloon while a concurrent small flow of N_2 was maintained, and the pressure of the system regulated by an oil bubbler. Upon saturation of the reaction mixture with CO, the colour changed from bright yellow, to pale yellow, pale pink to yield finally an almost colourless solution and CO was bubbled for another 15 minutes. The CO balloon was then removed and the contents of the Schlenk purged of CO by maintaining a N_2 flow through a venting needle for 1-2 minutes, upon which time the solution adopted a pale-yellow colouration. Filtration of the solution through a glass-microfibre filter-canulla yielded a pale yellow solution, volatiles were then removed in vacuum and when the volume had reduced to *ca* less than 1 mL, 10 mL of n-pentane were added to give an almost colourless precipitate, which was isolated by filtration and dried in vacuum to yield **5** as a pale yellow to colourless solid, that was stored in the glovebox. Yield: 75 mg (72 %). Yellow crystals of compound (5) were obtained by slow diffusion of n-pentane into a toluene solution of **5**. ^{1}H-NMR (300 MHz) δ($C_5D_5CD_3$): 8.15 (1H, dd, $^4J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 4.8 Hz, azaindole), 7.72 (1H, dd, , $^4J_{HH}$ = 1.4 Hz, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.70 (1H, m, azaindole), 7.66 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.55 (1H, dd, $^4J_{HH}$ = 1.1 Hz, $^3J_{HH}$ = 5.5 Hz, azaindole), 7.32 (1H, d, $^3J_{HH}$ = 3.3 Hz, azaindole), 7.25 (1H, d, $^3J_{HH}$ = 3.3 Hz, azaindole), 7.22 (1H, dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 7.9 Hz, azaindole), 7.14 (1H, dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 7.7 Hz, azaindole), 6.82 (1H, dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.7 Hz, azaindole), 6.66 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 6.40 (1H, dd, $^4J_{HH}$ = 0.7 Hz, $^3J_{HH}$ = 7.7 Hz, azaindole), 6.39 (1H, dd, $^4J_{HH}$ = 1.3 Hz, $^3J_{HH}$ = 7.9 Hz, azaindole), 6.29 (1H, d, $^3J_{HH}$ = 3.3 Hz, azaindole), 6.12 (1H, d, $^3J_{HH}$ = 3.3 Hz, azaindole), 5.61 (1H, ddd, $^3J_{HH}$ =10.3 Hz, $^3J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 10.3 Hz, C*H*=CH), 5.45 (1H, ddd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 10.3 Hz, $^3J_{HH}$ = 10.3 Hz, CH=C*H*), 2.11 (1H, m, cyclo-octenyl), 1.90 (2H, m, cyclo-octenyl), 1.74 (1H, m cyclo-octenyl), 1.6 (2H, m, cyclo-octenyl), 1.46 (1H. broad m, cyclo-octenyl), 1.20 (3H, m, cyclo-octenyl and Ir-C*H*), 0.85 (1H, broad m, C*H*H α-position to Ir-CH); ^{13}C{^{1}H}-NMR (125 MHz) δ($C_5D_5CD_3$): 173.1 (*C*O), 155.1, 153.1, 152.7, 142.8, 141.6, 138.2, 132.5, 131.6, 130.9, 129.4, 129.3, 128.2, 123.9, 122.4, 121.7, 115.9, 115.5, 114.8, 103.4, 103.2, 102.9 (azaindole, the two CH=CH of the cyclo-octenyl moiety are obscured from the solvent signals), 29.7, 29.3 27.9, 25.8, 24.8 (*C*H$_2$s of cyclo-octenyl), 22.7 (Ir-*C*H); ^{11}B{^{1}H}-NMR δ($C_5D_5CD_3$): -9.26 (s, $\Delta\nu_{1/2}$ = 27.9 Hz); ^{11}B-NMR δ($C_5D_5CD_3$): -9.26 (s); IR (neat): 1983.8 cm^{-1} ν(CO); IR (toluene): 2007.9 cm^{-1} ν(CO); IR (THF): 2011.7 cm^{-1} ν(CO); MS (ESI$^+$): 585.1 [M-cyclo-octenyl]$^+$, 693.2 [M+H]$^+$, 715.2 [M+Na]$^+$; Elem. Anal.: Found: C 53.89, H 4.20 N 11.30; Calc. for $C_{30}H_{28}BIrN_6O$.1/3 toluene: C 53.76, H 4.28, N 11.63. The boratrane complex **5** is obtained when the reaction is repeated in a THF/Et_2O (1:2) mixture, albeit in lower yield (50 %).

Ir(CO)(CNC_8H_9)(C_8H_{13}){κ^3-*NNB*-B(azaindoyl)$_3$) (6)

In the glovebox 30 mg of **5** (0.043 mmol) were weighed in a vial, and to this 5.7 mg (1 mol. eq.) of 2,6-dimethyl-phenylisocyanide were added. The two were dissolved in 0.5-0.6 mL of d^8-toluene and the reaction mixture transferred to a NMR tube and spectra recorded that showed complete conversion to **6**. The contents of the NMR tube were transferred in a Schlenk tube and volatiles removed in vacuum to give a yellow solid that was washed with pentane (5 mL) and dried in vacuum to give **6** as a pale yellow to off-white solid. Yield: 29 mg (81%). Colourless crystals of compound (**6**) were obtained by slow diffusion of n-pentane into a toluene solution of **6**. ^{1}H-NMR (300 MHz) δ($C_5D_5CD_3$): 8.26 (1H, dd, $^4J_{HH}$ = 2.2 Hz, $^3J_{HH}$ = 5.1 Hz, azaindole), 8.25 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7.7 Hz, azaindole), 8.20 (1H, d, $^3J_{HH}$ = 4.4 Hz, azaindole), 7.91 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.84 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7.7 Hz), 7.65 (1H, d, $^3J_{HH}$ = 2.9 Hz, azaindole), 7.32 (3H, m, azaindole and Ar-NC), 6.85 (2H, m, azaindole and Ar-NC), 6.71 (1H, d, 3.7 Hz, azaindole), 6.65 (2H, broad d, azaindole), 6.47 (2H, two d coinciding in the centre, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 2.9 Hz, azaindole), 6.43 (1H, m, azaindole), 6.37 (1H, m, azaindole), 5.65 (1H, m, C*H*=CH), 5.46 (1H, m, CH=C*H*), 2.4 (1H, broad, cyclo-octenyl), 2.25 (6H, s, C*H$_3$*), 2.18 (1H, m, cyclo-octenyl), 1.9 (5H, m, cyclo-octenyl), 1.53 (1H, broad, cyclo-octenyl), 1.35 (1H, m, cyclo-octenyl), 1.21 (1H, m, Ir-C*H*), 0.10 (1H, broad, C*H*H α-position to Ir-CH); ^{13}C{^{1}H}-NMR (125 MHz) δ($C_5D_5CD_3$): 172.5 (*C*O), 157.5, 157.2, 153.7, 152.7, 142.0, 141.8, 141.7, 135.3, 132.8, 131.3, 131.2, 129.7, 129.3, 129.2, 128.5, 128.4, 127.1, 125.6 123.4, 121.7, 121.4, 115.1, 114.8, 114.7, 103.6, 103.0, 100.5 (azaindole, aromatics of isocyanide and *C*H=*C*H), 45.7, 45.0, 31.7, 29.0 (*C*H$_2$s, cyclo-octenyl), 25.9 (*C*H$_2$ α to Ir-CH), 18.9 (2,6-(*C*H$_3$)$_2$-PhNC), 13.6 (Ir-*C*H). The isonitrile Ar-N*C* could not be located; ^{11}B{^{1}H}-NMR δ($C_5D_5CD_3$): 4.34 (s, $\Delta\nu_{1/2}$ = 119.4 Hz); ^{11}B-NMR δ($C_5D_5CD_3$): 4.34 (s); IR (neat): 2275.3 cm^{-1}, 2130.5 cm^{-1} ν(NC), 1987.3 cm^{-1} ν(CO); MS (ESI$^+$): 583.1 [M-ArNC- cyclo-octenyl]$^+$, 693.2 [M-ArNC+H]$^+$, 824.0 [M+H]$^+$; Elem. Anal.: Found: C 60.27, H 5.26 N 11.07; Calc. for $C_{39}H_{37}BIrN_7O$.toluene: C 60.39, H 4.96, N 10.72.

Ir(CO)(CNC$_4$H$_9$)(C$_8$H$_{13}$){κ^3-*NNB*-B(azaindoyl)$_3$) (7)

24.4 mg (0.035 mmol) of **5** were placed in the glove-box in a Young's NMR tube and were dissolved in approximately 0.6 mL of d^8-tol. (solvation can be aided by gentle heating). The solution was removed from the glove-box and 4.0 μL of ^{t}BuNC (d = 0.735 mg/μL; equal to 2.9 mg, 1 mol eq.) were added *via* a microsyringe at RT and the NMR spectra recorded that showed complete conversion to **7**. The contents of the NMR tube were transferred to a Schlenk and volatiles were removed in vacuum. The residue was washed with 5 mL of n-pentane and filtered, to give an off-white residue that was dried in vacuum. The volume of the filtrate was reduced to *ca.* half and then placed at -30 C to give a second crop of the product. Combined Yield: 22 mg (81 %). ^{1}H-NMR δ($C_6D_5CD_3$): 8.23 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 4.4 Hz, azaindole), 8.16 (2H, br. d, $^3J_{HH}$ = 4.4 Hz, azaindole), 7.89 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.83 (1H, dd, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 8.1 Hz, azaindole), 7.65 (1H, br. s, azaindole), 7.36 (1H, d, $^3J_{HH}$ = 3.7 Hz, azaindole), 7.32 (2H, d, $^3J_{HH}$ = 7.3 Hz), 6.84 (1H, m, azaindole), 6.71 (1H, $^3J_{HH}$ = 3.7 Hz, azaindole), 6.49-6.41 (4H, m, azaindole), 5.64 (1H, m, CH=C*H*), 5.50 (1H, m, C*H*=CH); 2.35 (1H, br. s, cyclo-octenyl), 2.02 (1H, br. s, cyclo-octenyl), 1.85 (3H, br. s, cyclo-octenyl), 1.71 (1H, br. s, cyclo-octenyl), 1.25 (3H, br. s, cyclo-octenyl + Ir-C*H*), 1.02 (9H, s, (C*H$_3$*)$_3$C-NC), 0.15 (1H, br. s, α CH*H* to Ir-CH); ^{13}C{^{1}H}-NMR δ($C_6D_5CD_3$): 172.3 (*C*O), 157.5, 157.3, 152.8, 141.9, 141.4, 141.1, 132.8, 131.9, 131.5, 131.2, 129.6, 129.3, 128.4, 127.1, 123.4, 121.6, 121.4, 115.0, 114.7, 114.6, 103.5, 102.9, 100.4 (azaindole and *C*H=*C*H), 57.1 ((CH$_3$)$_3$*C*-NC), 45.1, 44.3, 31.6 (*C*H$_2$s cyclo-octenyl), 29.8 ((*C*H$_3$)$_3$C-NC), 29.1, 25.8 (*C*H$_2$s cyclo-octenyl), 12.5 (Ir-*C*H) the ^{t}BuN*C* could not be located; ^{11}B{^{1}H}-NMR δ($C_6D_5CD_3$): 3.73 (s, $\Delta\nu_{1/2}$ = 120.7 Hz); ^{11}B-NMR δ($C_6D_5CD_3$): 3.73 (s, $\Delta\nu_{1/2}$ = 120.7 Hz); IR (neat): 2148.1 cm^{-1} ν(^{t}Bu-NC), 1993.7 ν(CO). MS (ESI)$^+$: 583.1 [M-^{t}BuNC-cylooctenyl]$^+$, 693.2 [M+H-^{t}BuNC]$^+$, 776.3 [M+H]$^+$, 858.3 [M+H+2MeCN]$^+$; Elem Anal. Found: C 55.85; H 5.40; N 11.38. Calc for $C_{35}H_{37}BIrN_7O$. ½ pentane: C 55.55; H 5.35; N 12.09.

Crystallography

The data for **5** and **6** were collected at 100 K and 173 K respectively, on a Bruker Kappa Apex II CCD detector diffractometer with a fine-focus sealed tube MoKa radiation source (λ = 0.71073 Å). The programs used for control and integration were APEXII, SAINT v7.34A and XPREP v2005/4.[S2] The crystal was mounted on a glass fibre with silicon grease. Solutions and refinements were performed using the Bruker SHELXTL software.[S3] All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were calculated and refined using a riding model.

The data collection parameters and refinement information are presented in Table 1. Anisotropic parameters, bond lengths and (torsion) angles for **5** and **6** are available from the cif file.

Selected bond lengths (Å) and angles (°) for 5 and 6

Complex 5: Ir(1)-N(6) 2.112(5), Ir(1)-N(2) 2.186(4), Ir(1)-B(1) 2.196(6), Ir(1)-C(1) 1.826(6), Ir(1)-C(23) 2.091(5), O(1)-C(1) 1.146(7), N(1)-B(1) 1.549(7), N(3)-B(1) 1.518(7), N(5)-B(1) 1.519(8); C(1)-Ir(1)-C(23) 91.4(2), C(23)-Ir(1)-N(6) 87.55(19), C(1)-Ir(1)-N(2) 93.5(2), N(6)-Ir(1)-N(2) 88.26(16), O(1)-C(1)-Ir(1) 175.3(5).

Complex 6: Ir(1)-C(30) 1.841(3), Ir(1)-C(31) 2.083(3), Ir(1)-N(1) 2.111(2), Ir(1)-C(22) 2.146(3), Ir(1)-N(3) 2.188(3), Ir(1)-B(1) 2.222(3), N(6)-B(1), 1.534(7), N(7)-C(31) 1.158(3), O(1)-C(30) 1.141(4), N(2)-B(1) 1.558(7), N(4)-B(1) 1.567(4); C(30)-Ir(1)-C(31) 93.33(18); C(31)-Ir(1)-N(1) 97.09(16), C(30)-Ir(1)-C(22) 93.43(12), C(31)-Ir(1)-C(22) 92.08(12), N(1)-Ir(1)-C(22) 84.59(10), C(30)-Ir(1)-N(3) 94.85(12), C(31)-Ir(1)-N(3) 96.05(12), N(1)-Ir(1)-N(3) 85.68(9), O(1)-C(30)-Ir(1) 179.6(3), N(7)-C(31)-Ir(1) 166.7(5).

Table 1 Crystallographic data for **5** and **6**.

Complex	**5**	**6**
Chemical Formula	$C_{30}H_{28}BIrN_6O$	$C_{46}H_{45}BIrN_7O$
Formula weight	691.59	914.90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
a / *Å*	9.2778(4)	9.7506(1)
b / *Å*	17.5888(7)	14.8856(2)
c / *Å*	15.9156(6)	14.0027(2)
α / °	90	90
β / °	93.999(2)	104.980(1)
γ / °	90	90
Z	4	2
T/K	100(2)	173(2)
μ / mm^{-1}	5.190	3.447
No. of data collected	23859	30024
No. of unique data	5925	11606
Goodness of fit on F^2	1.022	0.891
$R_{\text{int.}}$	0.0637	0.0363
Final $R(\|F\|)$ for $F_0 > 2\sigma(F_0)$	0.0385	0.0252
Final $R(F^2)$ for all data	0.0601	0.0305

References

S1. G. R. Owen, N. Tsoureas, A. Hamilton, A. G. Orpen, *Dalton Trans.,* 2008, 6039.
S2. Bruker-AXS, 2007; Bruker-AXS, 2005
S3. G. M. Sheldrick, *Acta Crystallogr., Sect. A*: *Found. Crystallogr.*, 2008, 64, 112.