Electronic Supporting Information for '*Synthesis and characterisation of group nine transition metal complexes containing new mesityl and naphthyl based azaindole scorpionate ligands*'

Gareth R. Owen, Nikolaos Tsoureas, Rebecca F. Hope, Yu-Ying Kuo and Mairi F. Haddow

The School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

Additional experimental details

General considerations

The solvents toluene, THF, DCM and acetonitrile were dried using a Grubbs' alumina system, and were kept in flame-dried 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 flame-dried Young's ampoule under N_2 over molecular sieves (4 Å). Deuterated toluene and C_6D_6 were degassed by three freeze-thaw cycles, dried by refluxing over Na or Na/benzophenone respectively for 12 hours, vacuum distilled and kept in a flame-dried Young's ampoule over 4 Å molecular sieves under N_2. Deuterated DCM was degassed by three freeze-thaw cycles, dried by refluxing over CaH_2 for 12 hours, vacuum distilled 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 ^{7}Li{^{1}H}-NMR spectra were recorded on a JEOL ECP300 spectrometer operating at 300 MHz (^{1}H). ^{1}H{^{11}B}-NMR spectra were recorded on a JEOL Lamda300 spectrometer operating at 300 MHz (^{1}H). ^{13}C{^{1}H}-NMR spectra and correlation experiments were recorded on a Varian VNMR S500 or JEOL ECP400 spectrometers. The spectra were referenced to an internal standard, 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 $BF_3{\cdot}OEt_2$. ^{7}Li{^{1}H}-NMR spectra were referenced externally to LiCl in D_2O.

Further characterisation of Li(MeCN)$_2$[^{Naphth}Bai]

Small quantities of the coordinated acetonitrile were found to dissociate in solution leading to two observable species in solution (in a ratio of *ca*. 85:15). See manuscript for further details. NMR δ ppm: ^{1}H ($CDCl_3$), 1.92 (s, 6 H, coordinated C*H*$_3$CN), 5.30–5.80 (v. br., 1H, B*H*), 6.38 (d, $^3J_{HH}$ = 3.4 Hz, 2H, aza-C*H*(3)], 6.84 [dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 4.9 Hz, 2H, aza-*CH*(5)], 7.11 [τ, J_{HH} = 7.9 Hz, 1H, nap-C*H*(6)], 7.23 [br., 2H, aza-C*H*(2)], 7.28 [br, 1H, nap-C*H*(2)], 7.32 [τd, J_{HH} = 7.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, nap-C*H*(7)], 7.39 [τ, J_{HH} = 7.3 Hz, 1H, nap-C*H*(3)], 7.73 [br., 2H, aza-C*H*(4)], 7.77 [two overlapping doublets, J_{HH} = 8.1 Hz, 2H, nap-C*H*(5) and -C*H*(4)], 7.82 [d, $^3J_{HH}$ = 7.9 Hz, 1H, nap-C*H*(8)], 7.88 [dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, aza-C*H*(6)]; ^{11}B{^{1}H}, (CD_2Cl_2), −8.9 (85%, $\Delta\nu_{1/2}$ = 97 Hz) and −4.0 (15%, $\Delta\nu_{1/2}$ = 94 Hz); ^{11}B, −8.9 (d, $^1J_{BH}$ = 74 Hz, $\Delta\nu_{1/2}$ = 194 Hz) and −4.0 (d, $^1J_{BH}$ = 92 Hz, $\Delta\nu_{1/2}$ = 194 Hz); ^{7}Li{^{1}H} (CD_2Cl_2), 5.3 (s, 85%) and 3.8 (s, 15%).

Selected data for Li[BH$_3$(mesityl)]•(THF)$_x$(Et$_2$O)$_y$

NMR (C_6D_6) δ ppm: ^{1}H, 1.32 [v. br., 1.1.1.1 q, 3H, $^1J_{BH}$ = 75Hz, B*H*$_3$(mesityl)], 2.37 (s, 3H, 4-Me), 2.73 (s, 6H, 2,6-Me), 7.09 [s, 2H, $C_6H_2(CH_3)_3$], ^{11}B{^{1}H}, −32.9 (s); ^{11}B, −32.9 (q, $^1J_{BH}$ = 76.2).

Selected data for Li[BH_3(naphthyl)]•$(THF)_x(Et_2O)_y$

NMR δ ppm: ^{1}H (CD_3CN), 1.44 [1:1:1:1 q, $^1J_{BH}$ = 79.4 Hz, B*H*$_3$(naphthyl)], 7.17 [dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, naphthyl], 7.29 [two overlapping m, 2H, naphthyl)], 7.39 [br d, $^3J_{HH}$ = 8.1 Hz, 1H, naphthyl], 7.49 [br m, 1H, naphthyl], 7.65 [m, 1H, naphthyl], 8.50 [unresolved dd, 1H, naphthyl-C*H*(8)]. ^{13}C{^{1}H}(CD_3CN), 123.1, 123.6, 124.6, 126.4, 128.4, 131.8, 133.3, 134.1, 140.1, carbon *ipso* to boron not observed. ^{11}B{^{1}H} (CD_2Cl_2), −28.0 (s); ^{11}B (CD_2Cl_2), −28.0 (q, $^1J_{BH}$ = 79 Hz).

Full ^{13}C{^{1}H} NMR assignments

Synthesis of Li[^{Mes}Bai]

NMR (CD_3CN) δ ppm: ^{13}C{^{1}H}, 20.9 [$C_6H_2(CH_3)_3$-*C*H$_3$(4)], 22.8 [$C_6H_2(CH_3)_3$-*C*H$_3$(2,6)], 99.7 [aza-*C*H(3)], 114.6 [aza-*C*H(5)], 123.9 [aza-*C*(7a)], 129.3 [aza-*C*H(4)], 129.9 [$C_6H_2(CH_3)_3$-*C*H(3,5)], 134.6 [aza-*C*H(2)], 134.9 [$C_6H_2(CH_3)_3$-*C*(2,6)], 141.8 [aza-*C*H(6)], 143.2 [$C_6H_2(CH_3)_3$-*C*(4)], 151.9 [aza-*C*(3a)], the carbon *ipso* to boron was not observed.

Synthesis of Li[^{Naphth}Bai]

NMR (CD_3CN) δ ppm: ^{13}C{^{1}H}, 99.9 [aza-*C*H(3)], 114.8 [aza-*C*H(5)], 123.8 [aza-*C*(3a)], 124.9 [nap-*C*H(6)], 125.3 [nap-*C*H(7)], 126.3 [nap-*C*H(3)], 127.0 [br., nap-*C*H(4)], 129.2 [nap-*C*H(5)], 129.3 [aza-*C*H(4)], 129.5 (B-$^{Naphth}C_{ispo}$), 130.0 [nap-C*H*(8)], 131.2 [br., nap-C*H*(2)], 134.1 [br., aza-*C*H(2)], 134.8 [nap-C(8a)], 138.5 [nap-C(4a)], 142.1 [aza-*C*H(6)], 152.4 [aza-*C*(7a)].

Rh(COD)(^{Mes}Bai) (4)

NMR (C_7D_8) δ ppm: ^{13}C{^{1}H}, 21.1 [$C_6H_2(CH_3)_3$-*C*H$_3$(4)], 24.7 [$C_6H_2(CH_3)_3$-*C*H$_3$(2,6)], 31.5 (COD), 75.7 (br., COD), 101.2 [aza-*C*H(3)], 114.1 [d, $^3J_{RhC}$ = 1.1 Hz, aza-*C*H(5)], 124.6 [aza-*C*(7a)], 128.5 [aza-*C*H(4)], 130.1 [aza-*C*H(2)], 133.6 [aza-*C*H(6)], 134.4 [$C_6H_2(CH_3)_3$-*C*(2,6)], 142.5 [$C_6H_2(CH_3)_3$-*C*(4)], 143.3 [$C_6H_2(CH_3)_3$-*C*H(3,5)], 151.9 [aza-*C*(3a)], carbon *ipso* to boron not observed.

Rh(COD)(^{Naphth}Bai) (5)

NMR (CD_2Cl_2) δ ppm: ^{13}C{^{1}H}, 31.7 (COD), 77.1 (br., COD), 101.2 [aza-*C*H(3)], 115.0 [aza-*C*H(5)], 124.5 [aza-*C*H(7a), 124.7 [nap-*C*H(6)], 125.1 [nap-*C*H(3)], 125.8 [nap-*C*H(7)], 127.2 [nap-*C*H(4)], 129.1 [two overlapping peaks, aza-*C*H(4) and nap-*C*H(5)], 129.5 [nap-*C*H(8)], 131.9 [nap-*C*H(2)], 133.5 [aza-*C*H(2)], 134.8 and 138.0 [nap-*C*(4a) and –*C*(8a)], 144.3 [aza-*C*H(6)], 144.7 [br., tentitively assigned as carbon *ipso* to boron], 152.8 [aza-*C*(3a)].

Ir(COD)(^{Mes}Bai) (6)

NMR (C_7D_8) δ ppm: ^{13}C{^{1}H}, 20.8 [$C_6H_2(CH_3)_3$-*C*H$_3$(4)], 24.1 [$C_6H_2(CH_3)_3$-*C*H$_3$(2,6)], 32.6 (COD), 57.5 (br., COD), 102.1 [aza-*C*H(3)], 114.3 [aza-*C*H(5)], 124.3 [aza-*C*(7a)], 128.4 [aza-*C*H(4), overlapping with solvent peaks observed in DEPT-135 experiment], 130.0 [aza-*C*H(2)], 132.2 [aza-*C*H(6)], 134.9 [$C_6H_2(CH_3)_3$-*C*(2,6)], 142.5 [$C_6H_2(CH_3)_3$-*C*(4)], 143.6 [$C_6H_2(CH_3)_3$-*C*H(3,5)], 153.0 [aza-*C*(3a)], carbon *ipso* to boron not observed; ^{11}B{^{1}H}, –0.8 ($\Delta\nu_{1/2}$ = 122 Hz).

Ir(COD)(^{Naphth}Bai) (7)

NMR (C_6D_6) δ ppm: $^{13}C\{^1H\}$, 33.0 (COD), 59.0 (br., COD), 103.0 [aza-*C*H(3)], 115.4 [aza-*C*H(5)], 125.0 [aza-*C*H(7a)], 125.4 [nap-*C*H(6)], 125.6 [nap-*C*H(7)], 126.0 [nap-*C*H(3)], 128.6 [nap-*C*H(4)], 129.3 [aza-*C*H(4)], 129.6 [nap-*C*H(8)], 129.7 [nap-*C*H(5)], 132.7 [nap-*C*H(2)], 133.0 [aza-*C*H(2)], 135.4 and 138.3 [nap-C(4a) and –C(8a)], 144.2 [aza-*C*H(6)], 154.4 [aza-*C*(3a)], carbon *ipso* to boron not observed.

Rh(NBD)(^{Mes}Bai) (8)

NMR (C_7D_8) δ ppm: $^{13}C\{^1H\}$, 21.1 [$C_6H_2(CH_3)_3$-*C*H_3(4)], 24.2 [$C_6H_2(CH_3)_3$-*C*H_3(2,6)], 41.6 [d, $^1J_{RhC}$ = 10.8 Hz, NBD], 48.4 [d, $^2J_{RhC}$ = 3.1 Hz, NBD], 58.9 [d, $^3J_{RhC}$ = 6.9 Hz, NBD], 101.5 [aza-*C*H(3)], 114.0 [aza-*C*H(5)], 124.1 [aza-*C*(7a)], 128.5 [aza-*C*H(4) overlapping with solvent observed by DEPT-135 experiment], 130.1 [$C_6H_2(CH_3)_3$-*C*H(3,5)], 133.1 [aza-*C*H(2)], 134.9 [$C_6H_2(CH_3)_3$-*C*(2,6)], 143.0 [aza-*C*H(6)], 142.7 [$C_6H_2(CH_3)_3$-*C*(4)], 152.1 [aza-*C*(3a)], carbon *ipso* to boron not observed.

Rh(NBD)(^{Naphth}Bai) (9)

NMR (CD_2Cl_2) δ ppm: $^{13}C\{^1H\}$, 43.1 [d, $^1J_{RhC}$ = 10.1 Hz, NBD], 48.8 [d, $^2J_{RhC}$ = 2.7 Hz, NBD], 59.5 [d, $^3J_{RhC}$ = 6.2 Hz, NBD], 101.5 [aza-*C*H(3)], 114.9 [aza-*C*H(5)], 124.1 [aza-*C*(7a), 125.0 [nap-*C*H(7)], 125.2 [nap-*C*H(6)], 125.8 [nap-*C*H(3)], 127.7 [nap-*C*H(4)], 128.9 [nap-*C*H(8)], 129.1 [aza-*C*H(4)], 129.2 [nap-*C*H(5)], 132.0 [nap-*C*H(2)], 133.0 [aza-*C*H(2)], 134.8 [nap-*C*(4a)], 137.8 [naphthyl–C(8a)], 142.6 [tentitively assigned as carbon *ipso* to boron], 142.8 [aza-*C*H(6)], 152.9 [aza-*C*(3a)].