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

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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 N₂ over molecular sieves (4 Å). Dry n-pentane (<0.05 ppm H₂O) was purchased from Fluka and was kept in a flame-dried Young’s ampoule under N₂ over molecular sieves (4 Å). Deuterated toluene and C₆D₆ 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 N₂. Deuterated DCM was degassed by three freeze-thaw cycles, dried by refluxing over CaH₂ for 12 hours, vacuum distilled and kept in a Young’s ampoule over 4 Å molecular sieves under N₂. ¹H-NMR, ¹¹B{¹H}-NMR, ¹³C{¹H}-NMR, ¹³B-NMR and ⁷Li{¹H}-NMR spectra were recorded on a JEOL ECP300 spectrometer operating at 300 MHz (¹H). ¹³B{¹H}-NMR spectra were recorded on a JEOL Lambda300 spectrometer operating at 300 MHz (¹³B). ¹³C{¹H}-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 (¹H) or the signals of the solvent (¹³C). ¹¹B{¹H}-NMR and ¹³B-NMR spectra were referenced externally relative to BF₃·OEt₂. ⁷Li{¹H}-NMR spectra were referenced externally to LiCl in D₂O.

Further characterisation of Li(MeCN)₂[NapthBai]

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: ¹H (CDCl₃), 1.92 (s, 6 H, coordinated CH₃CN), 5.30–5.80 (v. br., 1H, BH), 6.38 (d, ³JHH = 3.4 Hz, 2H, aza-CH(3)), 6.84 [dd, ³JHH = 7.3 Hz, ⁴JHH = 4.9 Hz, 1H, aza-CH(5)], 3.11 [τ, ⁶JHH = 7.9 Hz, 1H, nap-CH(6)], 7.23 [br., 2H, aza-CH(2)], 7.28 [br, 1H, nap-CH(2)], 7.32 [dd, ⁶JHH = 7.9 Hz, ²JHH = 1.2 Hz, 1H, nap-CH(7)], 7.39 [τ, ⁶JHH = 7.3 Hz, 1H, nap-CH(3)], 7.73 [br., 2H, aza-CH(4)], 7.77 [two overlapping doublets, ⁷JHH = 8.1 Hz, 2H, nap-CH(5) and -CH(4)], 7.82 [d, ³JHH = 7.9 Hz, 1H, nap-CH(8)], 7.88 [dd, ³JHH = 8.2 Hz, ⁴JHH = 1.2 Hz, 2H, aza-CH(6)]; ¹¹B{¹H}, (CD₂Cl₂), −8.9 (85%, Δν₁/₂ = 97 Hz) and −4.0 (15%, Δν₁/₂ = 94 Hz); ¹³B, −8.9 (d, ¹JBB = 74 Hz, Δν₁/₂ = 194 Hz) and −4.0 (d, ¹JBB = 92 Hz, Δν₁/₂ = 194 Hz); Li{¹H} (CD₂Cl₂), 5.3 (s, 85%) and 3.8 (s, 15%).

Selected data for Li[BH₃(mesityl)]·(THF)₆·Et₂O

NMR (CD₂Cl₂) δ ppm: ¹H, 1.32 [v. br., 1.1.1.1 q, 3H, ¹JBB = 75Hz, BH₃(mesityl)], 2.37 (s, 3H, 4-Me), 2.73 (s, 6H, 2,6-Me), 7.09 [s, 2H, C₆H₂(CH₃)₃], ¹¹B{¹H}, −32.9 (s); ¹³B, −32.9 (q, ¹JBB = 76.2).
Selected data for Li[BH₃(naphthyl)ₚ(THF)ₙ(Et₂O)ₙ]
NMR δ ppm: H (CD₃CN), 1.44 [1:1:1 q, J₉H = 79.4 Hz, BH₃(naphthyl)], 7.17 [dd, J₃H = 8.3 Hz, J₆H = 6.8 Hz, 1H, naphthyl], 7.29 [two overlapping m, 2H, naphthyl], 7.39 [br d, J₆H = 8.1 Hz, 1H, naphthyl], 7.49 [br m, 1H, naphthyl], 7.65 [m, 1H, naphthyl], 8.50 [unresolved dd, 1H, naphthyl-CH(8)]. ¹³C(¹H) (CD₃CN), 123.1, 123.6, 124.6, 126.4, 128.4, 131.8, 133.3, 134.1, 140.1, carbon ipso to boron not observed. ¹¹B(¹H) (CD₂Cl₂), −28.0 (s); ¹¹B (CD₂Cl₂), −28.0 (q, J₁H = 79 Hz).

Full ¹³C(¹H) NMR assignments

Synthesis of Li[MesBai]
NMR (CD₃CN) δ ppm: ¹³C(¹H), 20.9 [C₆H₂(CH₃)₃–CH₃(4)], 22.8 [C₆H₂(CH₃)₃–CH₃(2,6)], 99.7 [aza–CH(3)], 114.6 [aza–CH(5)], 123.9 [aza–C(7a)], 129.3 [aza–CH(4)], 129.9 [C₆H₂(CH₃)₃–CH(3,5)], 134.6 [aza–CH(2)], 134.9 [C₆H₂(CH₃)₃–C(2,6)], 141.8 [aza–CH(6)], 143.2 [C₆H₂(CH₃)₃–C(4)], 151.9 [aza–C(3a)], the carbon ipso to boron was not observed.

Synthesis of Li[NaphthBai]
NMR (CD₃CN) δ ppm: ¹³C(¹H), 99.9 [aza–CH(3)], 114.8 [aza–CH(5)], 123.8 [aza–C(3a)], 124.9 [nap–CH(6)], 125.3 [nap–CH(7)], 126.3 [nap–CH(3)], 127.0 [br., nap–CH(4)], 129.2 [nap–CH(5)], 129.3 [aza–CH(4)], 129.5 [B–NaphthCᵢ₃p₀], 130.0 [nap–CH(8)], 131.2 [br., nap–CH(2)], 134.1 [br., aza–CH(2)], 134.8 [nap–C(8a)], 138.5 [nap–C(4a)], 142.1 [aza–CH(6)], 152.4 [aza–C(7a)].

Rh(COD)ₙ(MesBai) (4)
NMR (C₇D₈) δ ppm: ¹³C(¹H), 21.1 [C₆H₂(CH₃)₃–CH₃(4)], 24.7 [C₆H₂(CH₃)₃–CH₃(2,6)], 31.5 (COD), 75.7 (br., COD), 101.2 [aza–CH(3)], 114.1 [d, Jᵢ₃Rac = 1.1 Hz, aza–CH(5)], 124.6 [aza–C(7a)], 128.5 [aza–CH(4)], 130.1 [aza–CH(2)], 133.6 [aza–CH(6)], 134.4 [C₆H₂(CH₃)₃–C(2,6)], 142.5 [C₆H₂(CH₃)₃–C(4)], 143.3 [C₆H₂(CH₃)₃–CH(3,5)], 151.9 [aza–C(3a)], carbon ipso to boron not observed.

Rh(COD)ₙ(NaphthBai) (5)
NMR (CD₂Cl₂) δ ppm: ¹³C(¹H), 31.7 (COD), 77.1 (br., COD), 101.2 [aza–CH(3)], 115.0 [aza–CH(5)], 124.5 [aza–CH(7a)], 124.7 [nap–CH(6)], 125.1 [nap–CH(3)], 125.8 [nap–CH(7)], 127.2 [nap–CH(4)], 129.1 [two overlapping peaks, aza–CH(4) and nap–CH(5)], 129.5 [nap–CH(8)], 131.9 [nap–CH(2)], 133.5 [aza–CH(2)], 134.8 and 138.0 [nap–C(4a) and –C(8a)], 144.3 [aza–CH(6)], 144.7 [br., tentitively assigned as carbon ipso to boron], 152.8 [aza–C(3a)].

Ir(COD)ₙ(MesBai) (6)
NMR (C₇D₈) δ ppm: ¹³C(¹H), 20.8 [C₆H₂(CH₃)₃–CH₃(4)], 24.1 [C₆H₂(CH₃)₃–CH₃(2,6)], 32.6 (COD), 57.5 (br., COD), 102.1 [aza–CH(3)], 114.3 [aza–CH(5)], 124.3 [aza–C(7a)], 128.4 [aza–CH(4), overlapping with solvent peaks observed in DEPT-135 experiment], 130.0 [aza–CH(2)], 132.2 [aza–CH(6)], 134.9 [C₆H₂(CH₃)₃–C(2,6)], 142.5 [C₆H₂(CH₃)₃–C(4)], 143.6 [C₆H₂(CH₃)₃–CH(3,5)], 150.0 [aza–C(3a)], carbon ipso to boron not observed; ¹¹B(¹H), −0.8 (Δν₁/₂ = 122 Hz).
**Ir(COD)(NaphthBai) (7)**

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

**Rh(NBD)(MesBai) (8)**

NMR (C_{7}D_{8}) δ ppm: $^{13}$C($^{1}$H), 21.1 [C_{6}H_{2}(CH_{3})_{3}-CH_{3}(4)], 24.2 [C_{6}H_{2}(CH_{3})_{3}-CH_{3}(2,6)], 41.6 [d, $^{1}$J_{RhC} = 10.8 Hz, NBD], 48.4 [d, $^{2}$J_{RhC} = 3.1 Hz, NBD], 58.9 [d, $^{3}$J_{RhC} = 6.9 Hz, NBD], 101.5 [aza-CH(3)], 114.0 [aza-CH(5)], 124.1 [aza-C(7a)], 128.5 [aza-CH(4) overlapping with solvent observed by DEPT-135 experiment], 130.1 [C_{6}H_{2}(CH_{3})_{3}-CH(3,5)], 133.1 [aza-CH(2)], 134.9 [C_{6}H_{2}(CH_{3})_{3}-C(2,6)], 143.0 [aza-CH(6)], 142.7 [C_{6}H_{2}(CH_{3})_{3}-C(4)], 152.1 [aza-C(3a)], carbon ipso to boron not observed.

**Rh(NBD)(NaphthBai) (9)**

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