

Supplementary Information

General procedures. All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun Labmaster glove box maintained at or below 1 ppm of O₂ and H₂O. Glassware was dried at 150 °C overnight. NMR data were recorded on a Varian Unity 400 spectrometer (400 MHz) at 22 °C. Diethyl ether, tetrahydrofuran and toluene were purified by the Glass Contour solvent purification system. Deuterated benzene was first dried over CaH₂, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200 °C under vacuum. 1-*tert*-Butylimidazole¹ and Me₃N:BHBr₂² were prepared and purified according to literature procedures. All peaks in the NMR spectra are referenced to residual CHCl₃ at δ 7.27 ppm or C₆D₅H at δ 7.16 ppm, respectively. For paramagnetic samples, the following are listed in parentheses: peak width at half-height in Hz, integration and assignment. Solution magnetic susceptibilities were determined by the Evans method.³ Electrospray mass spectral data were collected using a Waters-Micromass ZQ2000 Mass Spectrometer using CH₃CN as solvent.

Preparation of HB(^tBu-Im)₃(Br)₂: A solution of *tert*-butyl imidazole (2.00 g, 16.1 mmol) and Me₃N:BHBr₂ (1.24 g, 5.4 mol) in chlorobenzene (20 mL) was heated at reflux for 1 day. The reaction mixture was cooled to room temperature and the volatiles were removed *in vacuo* to afford a white solid. The solid was dissolved in CH₂Cl₂ (~20 mL) and diethyl ether added to give a white precipitate (1.98 g, 68% yield). Alternatively the CH₂Cl₂ solution can be cooled to -25 °C to give a white solid in ~60% yield.

Mp 273-275 °C. ¹H NMR (CDCl₃): δ 9.73 (s, 3H, HB(^tBu-Im)₃), δ 8.38 (s, 3H, HB(^tBu-Im)₃), δ 7.31 (s, 3H, HB(^tBu-Im)₃), δ 1.71 (s, 27H, HB(^tBu-Im)₃). ¹³C NMR (CDCl₃): δ 138 (HB(^tBu-C₃H₃N₂)₃), δ 125 (HB(^tBu-C₃H₃N₂)₃), δ 120 (HB(^tBu-C₃H₃N₂)₃), δ 60 (HB(Im-C(CH₃)₃)₃), δ 30 (HB(Im-C(CH₃)₃)₃). IR (KBr, cm⁻¹): 2474 (w, B-H). ESI⁺-MS 463 (C₂₁H₃₇N₆BBr⁺). Elemental analysis (%) calcd for C₂₁H₃₇N₆BBr₂: C 46.35, H 6.85, N 15.44; found: C 46.05, H 6.71, N 15.15.

Preparation of κ^3 -HB(^tBu-Im)₃MgBr: In the dry box, a solution of MeMgBr (2.14 mL, 6.43 mmol, 3.0 M soln. in Et₂O) was added to a slurry of HB(^tBu-Im)₃(Br)₂ (1.0 g, 1.84 mmol) in THF (15 mL). After a day of stirring at room temperature, the volatiles were removed *in vacuo* to give a white residue. The residue was extracted with copious amounts of toluene and filtered through a plug of Celite to give a colourless solution. The solution was cooled to -35 °C to yield a colourless solid (792 mg, 88%).

Mp 268-270°C. ¹H NMR (C₆D₆): δ 7.09 (s, 3H, HB(^tBu-Im)₃), 6.37 (s, 3H, HB(^tBu-Im)₃), 1.47 (s, 27H, HB(^tBu-Im)₃). ¹³C NMR (C₆D₆): δ 185, 124, 115, 56, 32. IR (KBr, cm⁻¹): 2469 (B-H). Elemental analysis (%) calcd for C₂₁H₃₄N₆BBrMg: C 51.94, H 7.05, N 17.31; found: C 52.17, H 7.17, N 17.10.

Preparation of κ^3 -HB(^tBu-Im)₃FeBr: In the dry box, solid FeBr₂ (46 mg, 206 μmol) was added to a solution of { κ^3 -HB(^tBu-Im)₃}MgBr (100 mg, 206 μmol) in THF (5 mL). After a day of stirring at room temperature, volatiles were removed *in vacuo*. The residue obtained was extracted with toluene, filtered through Celite, and pumped down to give a white solid (54 mg, 50% yield). Crystals suitable for X-ray determination were obtained from toluene at -35 °C. We have been unable to obtain satisfactory elemental analysis data for this complex.

Mp 110 °C (dec.). ¹H NMR (C₆D₆): δ 83 (412, 1H, HB(^tBu-Im)₃), 77 (75, 3H, HB(^tBu-Im)₃), 52 (105, 3H, HB(^tBu-Im)₃), -18 (173, 27H, HB(^tBu-Im)₃). IR (KBr, cm⁻¹): 2482 (w, B-H).

References:

1. A. E. Gridnev, I. M. Mihaltseva, *Synth. Commun.*, 1994, **24**, 1547.
2. M. A. Mathur, D. A. Moore, R. E. Popham, H. H. Sisler, S. Dolan, S. G. Shore, *Inorg. Synth.*, 1992, **29**, 51.
3. M. V. Baker, L. D. Field, T. W. Hambley, *Inorg. Chem.*, 1988, **27**, 2872.