

A new synthetic route to bulky “second generation” tris(imidazol-2-ylidene)borate ligands: synthesis of a four coordinate iron(II) complex†

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A bulky tripodal tris(carbene)borate ligand, prepared from 1-*tert*-butylimidazole, is cleanly transferred to iron(II) by a magnesium reagent.

The favourable properties of the bulky “second generation” tris(pyrazolyl)borate ligands have led to their widespread adoption in inorganic chemistry, with applications in fields such as C–H activation and metalloenzyme modeling chemistry.¹ In recent years, a number of tripodal ligands incorporating strongly donating atoms have been introduced. For example, the tris(phosphino)borate ligands $\text{PhB}(\text{CH}_2\text{PPh}_2)_3^-$ are able to stabilise unusual four-coordinate, low spin iron(II) and cobalt(II) centers.²

A relatively unexplored class of tripodal ligands is the tris(imidazol-2-ylidene)borates, which are composed of a facial array of bulky *N*-heterocyclic carbenes (Fig. 1).³ These ligands are topologically similar to the tris(pyrazolyl)borates, and it is anticipated that their steric, electronic and solubility properties can similarly be tailored by variation of the imidazole ring substituents. In particular, suitably bulky *N*-substituents are expected to lead to the creation of low coordinate metal complexes. Metal complexes of these ligands should have quite different electronic properties from those of the tris(pyrazolyl)borates due to the very strong σ -donor nature of *N*-heterocyclic carbenes.⁴

A number of tripodal ligands based on *N*-heterocyclic carbenes are known,^{5,6} but these differ in their size, flexibility and charge properties from tris(imidazol-2-ylidene)borates. In particular, the anionic nature and relative rigidity of the tris(imidazol-2-ylidene)borates are in contrast to the uncharged and flexible nitrogen-anchored tripodal *N*-heterocyclic carbene ligands pioneered by Meyer *et al.*⁶

Two tris(imidazol-2-ylidene)borate ligands have been reported (Fig. 1; R = Me, Et). These ligands were prepared by *N*-alkylation

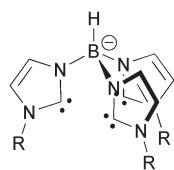


Fig. 1 Tris(imidazol-2-ylidene)borate ligands.

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of tris(imidazole)borate followed by low temperature deprotonation.⁷ However, reaction of these relatively unhindered ligands with divalent iron and cobalt precursors results in the formation of saturated six-coordinate complexes.⁷ It is expected that increasing the steric profile of the ligands by incorporating bulkier imidazole *N*-substituents will result in coordinatively unsaturated transition metal complexes. However, *N*-alkylation of imidazole by bulky substituents is often low yielding,⁸ presenting a limitation to the reported methodology. We report a new synthetic route that allows for the incorporation of bulkier substituents, and show that preparation of a low coordinate iron(II) complex is possible.

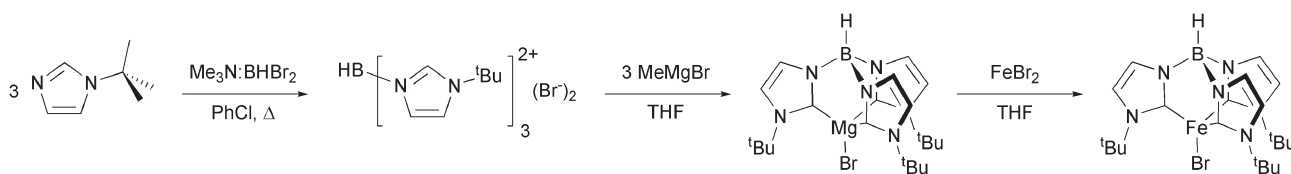
Heating 3 molar equivalents of 1-*tert*-butylimidazole (^tBuIm)⁹ with $\text{Me}_3\text{N}:\text{BHBr}_2^{10}$ in chlorobenzene at reflux for 18 h results in precipitation of the white dibromide salt $[\text{HB}(\text{tBuIm})_3]\text{Br}_2$ (Scheme 1).‡ This compound has been fully characterized.† A notable feature of the ¹H NMR spectrum is the highly shifted imidazole 2H proton, observed at δ 9.73 ppm.

Successful deprotonation of the borane dication to afford the tris(imidazol-2-ylidene)borate is strongly base-dependent. In our hands, bases typically used for the preparation of *N*-heterocyclic carbenes, including ^tBuLi, $\text{LiN}(\text{SiMe}_3)_2$ and KO^tBu result in decomposition. The only tractable material that we have isolated from these deprotonation attempts is *tert*-butylimidazole. However, we have found that MeMgBr cleanly deprotonates $[\text{HB}(\text{tBuIm})_3]\text{Br}_2$ in THF at room temperature and leads to $\text{HB}(\text{tBuIm})_3\text{MgBr}$, obtained from toluene in 88% yield as colourless crystals. We are unaware of other instances of Grignard reagents being used to prepare *N*-heterocyclic carbenes.

The structure of the magnesium complex was determined by X-ray crystallography (Fig. 2).§ The magnesium atom is four-coordinate, and bound to all three carbene carbons of the anionic borate ligand. The Mg–C bond lengths (average 2.21 Å) are consistent with other structurally characterized magnesium *N*-heterocyclic carbene complexes.¹¹ The large *tert*-butyl substituents ensure the formation of a mononuclear complex and prevent coordination of solvent molecules to the metal center.

Not surprisingly, the structure of this complex is similar to the closely related tris(*tert*-butylpyrazolyl)borate magnesium compound, $\text{HB}(\text{tBupy})_3\text{MgCl}$.¹² An interesting structural difference is that the longer Mg–C bond lengths in $\text{HB}(\text{tBuIm})\text{MgBr}$ (about 0.1 Å longer than the corresponding Mg–N bond lengths in $\text{HB}(\text{tBupy})\text{MgCl}$) result in greater distortion from ideal tetrahedral geometry at the magnesium center (the C–Mg–C bond angles are closer to 90°).

The solution ¹H NMR spectrum of $\text{HB}(\text{tBuIm})_3\text{MgBr}$ is consistent with the solid state structure.¶ Most notably, only two signals are observed for the imidazol-2-ylidene ring protons, at



Scheme 1

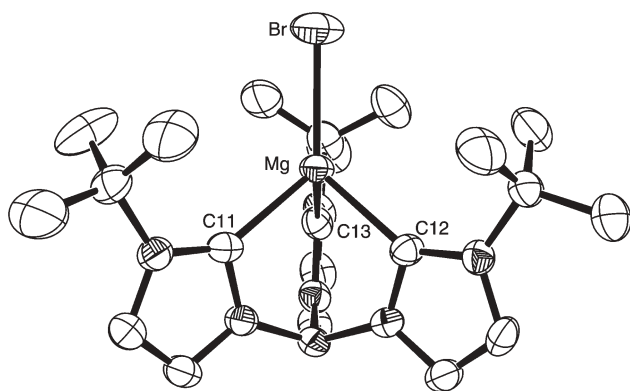


Fig. 2 Molecular structure of $\text{HB}(\text{tBuIm})_3\text{MgBr}$. Hydrogen atoms are not shown, thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles ($^\circ$): Mg–Br 2.449(1), Mg–C11 2.216(3), Mg–C12 2.208(3), Mg–C13 2.199(3), C11–Mg–C12 89.9(1), C11–Mg–C13 92.3(1), C12–Mg–C13 89.8(1), C11–Mg–Br 124.68(9), C12–Mg–Br 126.34(9), C13–Mg–Br 123.35(9).

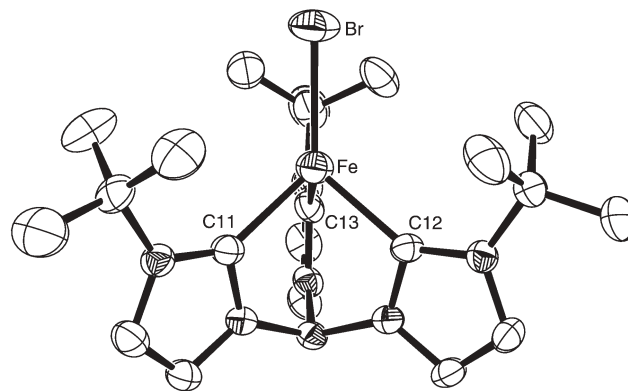


Fig. 3 Molecular structure of $\text{HB}(\text{tBuIm})_3\text{FeBr}$. Hydrogen atoms are not shown, thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles ($^\circ$): Fe–Br 2.4432(6), Fe–C11 2.135(3), Fe–C12 2.123(3), Fe–C13 2.127(3), C11–Fe–C12 91.1(1), C11–Fe–C13 90.6(1), C12–Fe–C13 93.1(1), C11–Fe–Br 125.85(9), C12–Fe–Br 125.63(8), C13–Fe–Br 122.91(9).

δ 7.09 and 6.37 ppm. The carbene carbons are characterised by a resonance at δ 185 ppm in the ^{13}C NMR spectrum. While the B–H group is observed in the IR spectrum ($\nu_{\text{B-H}} = 2469 \text{ cm}^{-1}$), it is not observed in the ^1H NMR spectrum presumably since it is broadened into the baseline. The complex is stable for months at ambient temperature, provided it is stored in an inert atmosphere.

We have found the magnesium complex to be an effective and clean ligand transfer reagent. Accordingly, the room temperature reaction of $\text{HB}(\text{tBuIm})_3\text{MgBr}$ with a slurry of FeBr_2 in THF leads to the formation of colourless $\text{HB}(\text{tBuIm})_3\text{FeBr}$, isolated in 50% yield. We attribute the moderate yield to the relatively poor solubility of the complex in nonpolar solvents, as no other products are detected in the ^1H NMR spectrum of the crude reaction mixture.

The X-ray crystal structure confirms the monomeric, four-coordinate nature of the iron atom in $\text{HB}(\text{tBuIm})_3\text{FeBr}$ (Fig. 3). The complex is isostructural with $\text{HB}(\text{tBuIm})_3\text{MgBr}$, with the tris(imidazol-2-ylidene)borate ligand coordinating to the iron center in a tridentate fashion, and the bulky *tert*-butyl groups helping to create a pseudotetrahedral environment at iron. There is no evidence for agostic interactions as the closest intramolecular $\text{Fe}\cdots\text{H}-\text{C}$ contact is 2.87 Å.

This complex is one of the few iron(II) complexes based on ligands that contain *N*-heterocyclic carbenes.¹³ The Fe–C bond lengths in $\text{HB}(\text{tBuIm})_3\text{FeBr}$ are similar to these other complexes. Compared to the closest analogous tris(pyrazolyl)borate iron complex, $\text{HB}(\text{Bupz})_3\text{FeCl}$,¹⁴ there are similar structural differences as those observed above for $\text{HB}(\text{tBuIm})_3\text{MgBr}$. Due to the slightly longer bond lengths in $\text{HB}(\text{tBuIm})_3\text{FeBr}$, the C–Fe–C bond angles are compressed and closer to 90° than in the tris(pyrazolyl)borate complex.

The solution structure is consistent with C_{3v} symmetry. In the ^1H NMR spectrum, four paramagnetically shifted resonances are observed. On the basis of integration, three of these can be assigned to protons from the three equivalent imidazol-2-ylidene rings, with the fourth resonance attributed to the B–H group. The solution magnetic moment, measured by the Evans' method¹⁵ ($\mu_{\text{eff}} = 4.9(3) \mu_{\text{B}}$), is consistent with mononuclear $S = 2$ iron.

In summary, our new synthetic route greatly expands the potential of the tris(imidazol-2-ylidene)borate ligand class. In principle, the accessibility of these ligands is limited only by availability of the starting imidazole,¹⁶ making possible the customization of ligand steric and electronic characteristics. Further studies of complexes supported by these interesting ligands are in progress.

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Notes and references

‡ $\text{HB}(\text{tBuIm})_3\text{Br}_2$: Yield 68% based on $\text{Me}_3\text{N:BHBr}_2$. Mp 273–275 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3 , 23 $^\circ\text{C}$) δ 9.73 (s, 1H, C2–H); 8.38 (s, 1H, C3/4–H), 7.31 (s, 1H, C3/4–H), 1.71 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 23 $^\circ\text{C}$) δ 138, 125, 120, 60, 30. IR (KBr) 2474 cm^{-1} (B–H). ESI⁺-MS 463 ($\text{C}_{21}\text{H}_{37}\text{N}_6\text{BBR}^+$). Anal. found: C 46.05, H 6.71, N 15.15. $\text{C}_{21}\text{H}_{37}\text{N}_6\text{BBR}_2$ requires C 46.35, H 6.85, N 15.44.

§ *Crystal Data*. For $\text{HB}(\text{tBuIm})_3\text{MgBr}$: $\text{C}_{28}\text{H}_{42}\text{BBR}\text{MgN}_6$, $M = 577.71$, orthorhombic, $a = 18.848(2)$, $b = 16.393(2)$, $c = 10.150(1)$ Å, $U = 3136.0(5)$ Å³, $T = 123(2)$ K, space group $Pna2_1$, $Z = 4$, $\mu(\text{Mo-K}\alpha) 1.357 \text{ mm}^{-1}$, 35582 reflections collected, 7513 unique ($R_{\text{int}} = 0.0509$) which were used in all calculations. The final $wR(F^2)$ was 0.1253 (all data). CCDC 270734. For $\text{HB}(\text{tBuIm})_3\text{FeBr}$: $\text{C}_{28}\text{H}_{42}\text{BBR}\text{FeN}_6$, $M = 609.25$, orthorhombic, $a = 18.912(2)$, $b = 16.268(2)$, $c = 10.125(1)$ Å, $U = 3114.9(5)$ Å³, $T = 123(2)$ K, space group $Pna2_1$, $Z = 4$, $\mu(\text{Mo-K}\alpha) 1.793 \text{ mm}^{-1}$, 35273

reflections collected, 7489 unique ($R_{\text{int}} = 0.0375$) which were used in all calculations. The final $wR(F^2)$ was 0.1331 (all data). CCDC 270735. See <http://dx.doi.org/10.1039/b505985b> for crystallographic data in CIF or other electronic format.

¶ $\text{HB}(\text{tBuIm})_3\text{MgBr}$: Yield 88% based on $\text{HB}(\text{tBuIm})_3\text{Br}_2$. Mp 268–270 °C ^1H NMR (400 MHz, C_6D_6 , 23 °C) δ 7.09 (s, 3H, C3/C4-H), 6.37 (s, 3H, C3/4-H), 1.47 (s, 27H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 23 °C) δ 185, 124, 115, 56, 32. IR (KBr) 2469 cm^{-1} (B-H). Anal. found: C 52.17, H 7.17, N 17.10. $\text{C}_{21}\text{H}_{37}\text{N}_6\text{BBr}_2$ requires C 51.94, H 7.05, N 17.31.

|| $\text{HB}(\text{tBuIm})_3\text{FeBr}$: Yield 50% based on $\text{HB}(\text{tBuIm})_3\text{MgBr}$. Mp 110 °C (dec.). ^1H NMR (400 MHz, C_6D_6 , 23 °C) δ 83 (1H, B-H), 77 (3H, Im-H), 52 (3H, Im-H), -18 ($\text{C}(\text{CH}_3)_3$). IR (KBr) 2482 cm^{-1} (B-H) $\mu_{\text{eff}} = 4.9(3) \mu_{\text{B}}$.

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