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COMMUNICATION

The elusive tripodal tris(2-pyridyl)borate ligand: a strongly coordinating tetraarylborate†‡

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Tris(2-pyridyl)borates are introduced as a new robust and tunable "scorpionate"-type ligand family. A facile synthesis of this hitherto unknown ligand and its complexation to Fe(II) are described; the optical and electrochemical properties of the resulting iron complex are compared to complexes derived from tris(pyrazolyl)borate, tris(2-pyridyl)aluminate, and corresponding charge-neutral ligands.

Since Trofimenko first introduced tris(2-pyrazolyl)borates (Tp, **A** in Chart 1) in 1966, they have evolved into one of the most useful classes of ligands in modern coordination chemistry.[1] They are commonly referred to as "scorpionates" to reflect their distinct coordination geometry and the potency in forming complexes with essentially every metal in the periodic table. Consequently, these and related ligands have found widespread applications ranging from homogeneous catalysis to bioinorganic chemistry and materials science.[2]

While the Tp ligands offer advantages in terms of their ease of synthesis and tunability, the stability of the B–N bonds has often been a concern.[3] Ligand rearrangements illustrate the relatively labile nature of the polar B–N bonds. As an example, the $HB(3\text{-}^iPrpz)_3$ ligand was shown to undergo 1,2-borotropic shifts in one of its pyrazolyl (*pz*) substituents to yield the 5-isopropylpyrazolyl isomer.[3b] Another concern is that decomposition with formation of the parent pyrazoles is quite common and often catalyzed by Lewis acids or Brønsted acids.[3a,c] On the contrary, boron forms strong and significantly less polar bonds to carbon, an aspect that has enabled organoborane chemistry as an important field in modern synthesis.[4] Indeed, tetraarylborates, and especially those containing electron-withdrawing fluorine substituents as in **B**, are among the most stable and weakly coordinating anions.[5] They are widely utilized in applications where reactive positively charged species are encountered, for instance in Ziegler–Natta type olefin polymerization as well as in electrochemical processes.[6]

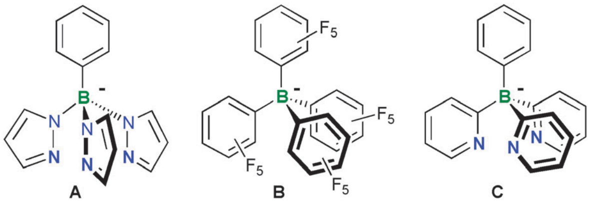

Chart 1 Comparison of strongly coordinating tris(pyrazolyl)borates, weakly coordinating arylborates and the targeted tris(2-pyridyl)borates.

Based on these considerations, a promising ligand design is to place 2-pyridyl (py) groups on boron to form tris(2-pyridyl)borate ligands **C**. While tris(2-pyridyl) tripod ligands have been synthesized with a variety of different bridge atoms (*e.g.* C, Si, Sn, Pb, N, P, As, Al, In),[7] tris(2-pyridyl)borate ligands have not been reported to date.[8–12] In addition to the expected enhanced stability, significant differences between the coordination behavior of tris(pyrazolyl)borate and tris(2-pyridyl)borate ligands can be expected, considering that pyridine is a better σ donor than pyrazole. The successful preparation of tris(2-pyridyl)borates is not only expected to lead to new catalytic applications, but they could also prove highly versatile as building blocks for functional supramolecular polymers. N-based tridentate ligands such as terpyridines and bis(imidazolyl)pyridines have had a dramatic impact on supramolecular chemistry and polymer science.[13]

An obstacle that possibly derailed earlier attempts at the preparation of tris(2-pyridyl)borates is that highly Lewis acidic haloboranes RBX_2 (X = Br, Cl), which are commonly reacted with arylating agents ArM (M = Li, Cu, MgX, SnR_3, HgR) to synthesize arylboranes and borates, readily form Lewis acid–base complexes with pyridines.[4] Moreover, ether solvents tend to react with haloboranes to give dialkoxy-substituted boranes, which in our hands proved to be not sufficiently reactive to form the desired tris(2-pyridyl)borate species. Hence, we decided to explore the use of an isolable reagent that can be reacted in non-coordinating solvents. We turned to 2-PyMgCl, which can be prepared on a >100 g scale by metal-halogen exchange of *i*-PrMgCl and 2-bromopyridine in THF and isolated as a white crystalline solid. According to a single crystal X-ray analysis,[14] the latter consists of a dimeric species with 3 coordinated molecules of THF and another molecule of THF that is located in 1D-channels along the crystallographic *c*-axis.† Importantly, this Grignard reagent proved to be soluble and reasonably stable in toluene and CH_2Cl_2 based on ^1H NMR analyses.

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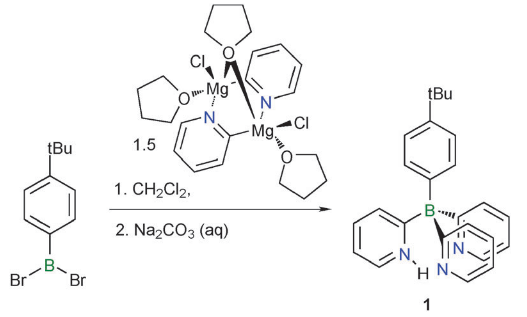
‡ Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c2cc33059h



Scheme 1 Synthesis of the tris(2-pyridyl)borate ligand **1**.

To prepare the borate ligand **1** (Scheme 1), a solution of *t*-butylphenyl dibromoborane[15] in CH_2Cl_2 was slowly added to 2-PyMgCl in CH_2Cl_2 at RT, and the mixture was stirred for an additional 5 h. An aqueous Na_2CO_3 solution was then added and the product extracted into CH_2Cl_2. Column chromatography on NEt_3-deactivated silica gel, followed by crystallization from toluene gave the analytically pure ligand **1** in its protonated form as a colorless solid in 54% yield.

The ligand was analyzed by multinuclear NMR and the assignments of the pyridine signals were confirmed by COSY, NOESY, and HMQC techniques. The ^{11}B NMR shows a sharp singlet at −10.8 ppm, which is in the region expected for tetraarylborates, while a singlet in the ^{1}H NMR at 19.5 ppm confirms the presence of a nitrogen-bound proton. The ^{13}C NMR exhibits characteristic quartets (J = 50 Hz) near 155 and 185 ppm, which are due to coupling of the ^{11}B nucleus to the quaternary phenyl and pyridyl carbons, respectively. The structure of the ligand was further confirmed by single-crystal X-ray diffraction analysis. One of two crystallographically independent, but otherwise very similar molecules in the unit cell is displayed in Fig. 1. For each molecule, two of the pyridyl rings are almost in a coplanar arrangement with small dihedral angles of 18.95 and 21.19°, respectively, as a result of hydrogen bonding between the pyridyl-bound proton of one of the pyridyl rings and the nitrogen of the other.[16] The B–C distances to the phenyl rings (1.628, 1.638 Å) are similar to those to the pyridyl substituents (1.635–1.643 Å) and in the range typically observed for arylborates, as are the C–B–C angles (106.2–113.5°). This confirms the absence of any significant steric strain.

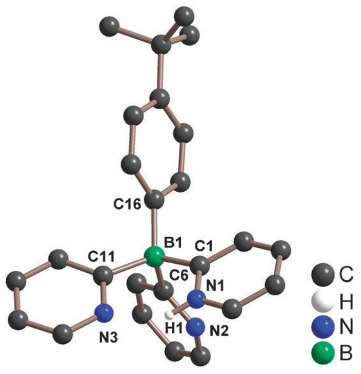


Fig. 1 Ball-and-stick representation of the X-ray structure of the ligand **1** (hydrogen atoms are omitted except for the acidic proton H1).

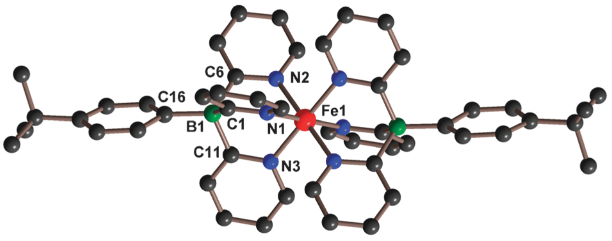


Fig. 2 Ball-and-stick representation of the X-ray structure of the Fe(II) complex **2** (hydrogen atoms are omitted or clarity).

We next explored the ability of **1** to form complexes with transition metal ions. Treatment with $FeCl_2$ in a THF/MeOH mixture in the presence of NEt_3 gave a red solid that was purified by column chromatography and recrystallized from toluene. The resulting complex Fe{(^{t}BuPh)B(2-py)$_3$}$_2$ (**2**, see Fig. 2) showed a sharp peak in the ^{11}B NMR at −7.5 ppm. While the ^{11}B NMR shifts of **1** and **2** are fairly similar, the pattern of the pyridyl rings in the ^{1}H NMR changed dramatically as a result of mutual shielding effects of the six pyridyl rings around the central Fe atom. Thus, the pyridyl protons in the *ortho* and *meta*-positions to N experience large upfield shifts from 8.49 and 7.10 to 7.11 and 6.44 ppm, respectively. Conversely, the phenylene protons are strongly shifted downfield.

Single crystals of **2** were grown by slow evaporation of a toluene solution. Coordination of the tris(2-pyridyl)borate moieties as tridentate ligands to the metal center does not lead to dramatic changes in the ligand architecture (Fig. 2). The iron atom lies on a crystallographic inversion center and adopts a slightly distorted octahedral geometry. Two of the Fe–N bonds are of similar length (1.9902(13), 1.9880(13) Å), whereas the third is significantly shorter (1.9685(13) Å). The N–Fe–N angles are close to 90° with a maximum deviation of 0.27°. The pyridine nitrogens of one ligand are arranged coparallel to those of the second ligand at a distance of 2.29 Å, similar as in the aluminate complex Fe{MeAl(2-py)$_3$}$_2$[17] (2.19 Å). The phenyl rings are also positioned in a coparallel arrangement at a distance of 0.97 Å from one another.

The Fe–N bond lengths are indicative of the ligand field strength, which determines the spin state and hence the optical and magnetic properties of Fe(II) complexes. The Fe–N bonds of 1.9685(13)–1.9902(13) Å in **2** are comparable to the ones in neutral tripodal pyridyl ligands, *e.g.* Fe–N = 1.970(5)–1.995(5) Å for [Fe{N(2-py)$_3$}$_2$]$^{2+}$[18] and Fe–N = 1.947(2)–1.954(2) Å for [Fe{HC(2-py)$_3$}$_2$]$^{2+}$[19] Both of these complexes were reported to be diamagnetic even at room temperature.[19] In contrast, the Fe–N bond lengths in the complex Fe{MeAl(2-py)$_3$}$_2$[17] are significantly longer at 2.054(3) Å, and this complex proved to be paramagnetic.

The comparatively short Fe–N bonds in **2** suggest that the complex is diamagnetic in the solid state. Based on the NMR data, **2** is diamagnetic also in solution, consistent with a low spin configuration. UV-vis measurements were performed in CH_2Cl_2 to further explore this aspect. The absorption maxima at *ca.* 480 and 425 (sh) nm (Fig. 3a) can be assigned to M → L charge transfer (CT). The corresponding cationic Fe(II) complexes [Fe{HC(2-py)$_3$}$_2$][NO$_3$]$_2$ (439, 370 nm) and [Fe{PO(2-py)$_3$}$_2$]-[NO$_3$]$_2$ (465, 385 nm) show similar absorption bands, but at comparatively higher energy.[19] Importantly, the optical spectra are quite different from those reported for the paramagnetic complex Fe{MeAl(2-py)$_3$}$_2$[17] (510, 431, 366 nm in THF).

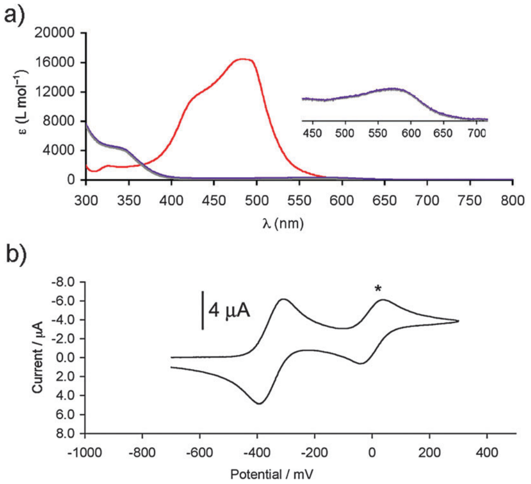


Fig. 3 (a) UV-vis spectra of complexes **2** (red) and [$\mathbf{2}^+$][$FeCl_4$] (purple). (b) Cyclic voltammogram for complex **2** (1×10^{-3} M, 0.1 M [Bu_4N]PF_6 in CH_2Cl_2, scan rate 100 mV s^{-1}; *vs.* Fc/Fc^+ (*)).

The redox properties of **2** were studied by cyclic voltammetry (Fig. 3b). A reversible redox process at −350 mV *vs.* Fc/Fc^+ indicates that **2** is far more electron-rich than ferrocene and even more easily oxidized than the Tp complex Fe{$HB(pz)_3$}$_2$ (−270 mV *vs.* Fc/Fc^+),[20] consistent with the anticipated strong σ-donor character of the ligand. Preparative oxidation of **2** with aqueous $FeCl_3$ resulted in a dark purple solid. UV-Vis analysis of the product ([$\mathbf{2}^+$]$FeCl_4$) in CH_2Cl_2 revealed a weak, broad band at 574 nm (ε = 370 cm^{-1} M^{-1}), in addition to a stronger absorption at 340 nm; the lower energy absorption at 574 nm is comparable in energy to those reported for [Fe{$HB(pz)_3$}$_2$]PF_6 (556 nm)[20] and [Fe{$HC(pz)_3$}$_2$][ClO_4]$_3$ (466, 560 (sh) nm[19]) and assigned to a dd transition. A single crystal X-ray analysis (Fig. 4) revealed a structure that is quite similar to that of the neutral complex **2**, except for that the Fe–N bond lengths in [$\mathbf{2}^+$] are less evenly distributed from 1.965(3) Å to 2.011(3) Å, reflecting significant distortion of the octahedral geometry.

In conclusion, we have introduced the first examples of tris(2-pyridyl)borate ligands and their metal complexes. Given the high stability, the strongly donating ability toward main group and transition metals, and the possibly for modular synthesis and ligand fine-tuning using different pyridyl derivatives, we anticipate broad applications of this new ligand class in catalysis, bioinorganic chemistry, and in the field of supramolecular polymer chemistry.

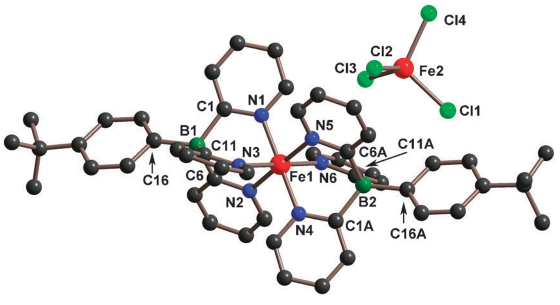


Fig. 4 Ball-and-stick representation of the X-ray structures of [$\mathbf{2}^+$]$FeCl_4$ (hydrogen atoms are omitted for clarity).

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