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Low-Coordinate Iron Complexes Based on Bis(pyrazolyl)borate and Their Reactivity

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Preparation routes for several sodium salts of diphenylbis-(pyrazolyl)borates with bulky substituents are described. For a potential modelling of α-keto-acid-dependent nonheme iron enzymes, mononuclear iron compounds containing those bis(pyrazolyl)borates as ligands were synthesised and structurally characterised. The iron centres are four-coordinate (in one case only three-coordinate) thus offering room for the binding of exogenous ligands. However, reactivity studies with carboxylates and O_2 have revealed nonuniform behaviour, and the identification of a side product in one case, combined with subsequent ESI-MS studies, demonstrated that a pronounced sensitivity of the B–N bonds towards oxo nucleophiles could be a possible reason.

Introduction

Iron-containing proteins are subdivided into three different categories: heme, iron–sulfur and nonheme. Nonheme enzymes typically bind iron by using only amino acid residues, and one of the best-studied classes are those that activate dioxygen.[1] Mononuclear representatives often contain two histidines and one additional amino acid residue (carboxylate, phenolate) in the coordination sphere of an iron(II) centre, while the three other sites are available for binding exogenous ligands such as solvent, substrate, cofactor and/or O_2. The flexibility towards the binding of exogenous ligands accounts for the diversity of reactions catalysed by this superfamily.[1] It includes, for instance, the α-keto-acid-dependent enzymes which require an α-keto acid to carry out a broad range of oxidative transformations with O_2. After O_2 binds to the Fe^{II} centre, it attacks the carbonyl C atom of the α-keto acid, leading to CO_2 release and formation of an Fe^{IV}=O intermediate, which is capable of performing hydroxylations, C–C desaturations etc.[1] Initial attempts to create functional molecular models for this kind of prosthetic group employed the tris[(6-methyl-2-pyridyl)methyl]amine (6-Me_3-tpa) ligand, which was coordinated to an Fe^{II} centre together with benzoylformato [$^{-}O_2C$–C(=O)–Ph, BF] as the sacrificial cofactor.[2] On oxygen treatment, this complex was shown to oxidise PPh_3 and 2,4-di-*tert*-butylphenol, but these reactions took a period of days because the six-coordinate precursor did not offer any vacant site for O_2 binding. Hence, tridentate hydrotris(pyrazolyl)borate ligands ($Tp^{R,R'}$) were examined subsequently in analogous reactions. A corresponding complex, [Fe^{II}($Tp^{tBu,iPr}$)(BF)], proved to be unreactive towards O_2 despite the open coordination site, and this has been rationalised in terms of the steric bulk, induced by the three *tert*-butyl substituents in the 3-positions of the pyrazole units, that impedes access to O_2.[3] This is supported by the observation that the analogous complex, [Fe^{II}-($Tp^{Ph,Ph}$)(BF)], in which the *tert*-butyl groups have been replaced by phenyl residues, becomes decarboxylated {Fe[O_2C–C(=O)–Ph] → Fe(O_2C–Ph)} in the presence of O_2 within an hour.[4] More interestingly, [Fe^{II}($Tp^{Me,Me}$)(BF)] treated with O_2 could be used to epoxidise *cis*-stilbene[5] while *trans*-stilbene was not epoxidised due to steric congestion. These examples show that decreasing the denticity of the ligand, as well as the reduction of the steric bulk within a ligand, leads to an increase in the reactivity of functional models for α-keto-acid-dependent enzymes. A very recent study showed that this is not the case if, at the same time, large groups are introduced at the α-keto carboxylate. In order to model α-keto-acid-dependent nonheme iron halogenases (the latter additionally contain a halido ligand in the prosthetic groups[6]), sterically bulky α-keto carboxylates were coordinated to $LFeCl^+$ complex metal fragments (L = diamine or bipyridine derivatives).[7] While the compounds obtained closely model the active site structure, oxidative decarboxylations did not occur in the presence of O_2.[6] Hence, the steric hindrance useful for structural modelling prohibited functional mimicry of the halogenase.

With regard to the former studies[2–5] employing tpa and $Tp^{R,R'}$, we have contemplated a further decrease in the coordination sites required by the ligand employed by utilising bis(pyrazolyl)borate ligands ($Bp^{R,R'}$) which nicely mimic

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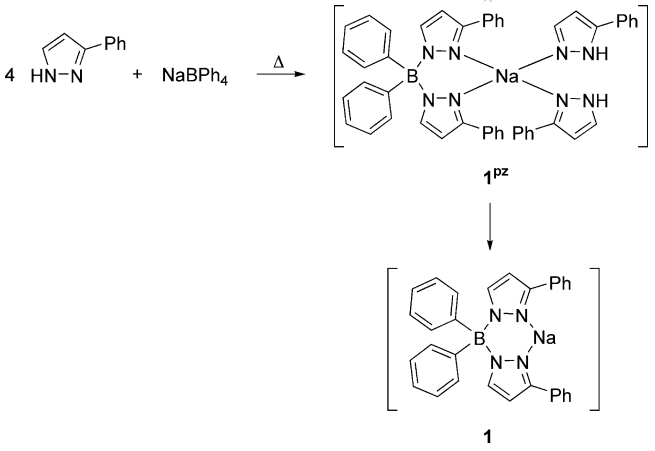
the two histidines bound to iron within the native enzymes. Being aware that, at the same time, this leads to a decrease in complex stability, which might reach a level interfering with productivity, we have carried out a corresponding investigation on the $Bp^{R,R'}Fe/BF/O_2$ system, and we report the results herein.

Results and Discussion

Ligand Synthesis

Some mononuclear iron complexes containing the unsubstituted dihydridobis(pyrazolyl)borate ligand have been reported already. These include the carbonyl complexes $[Bp_2Fe(CO)_2]$[8] and $[(C_3F_7)Fe(CO)_3Bp]$,[9] the phenanthroline complex $[FeBp_2phen]$,[10] the bis(pyridine) complex $[FeBp_2bipy]$[10] as well as the bis(trimethylphosphane) complex $[Fe(COMe)Bp(CO)(PMe_3)_2]$.[11] Furthermore, treating $FeCl_2{\cdot}4H_2O$ with {dihydrobis(3-*tert*-butyl-1-pyrazolyl)-borato}thallium, Paneque and Carmona obtained the bis(dihydrobispyrazolylborate) complex $[Fe(Bp^{tBu})_2]$.[12] In order to prevent any unwanted interaction of the metal with the hydridoborate units, such as the agostic interaction of the metal centre with pseudoaxial B–H or B–C–H units, we decided to use diphenyl- instead of dihydridobis(pyrazolyl)-borate ligands,[13] and as the residues in the 3-position of the pyrazole units we chose phenyl, too, firstly in order to shield the iron centre to some extent (as in the case of the corresponding Tp compounds mentioned above) and secondly to avoid the formation of homoleptic complexes such as the one reported by Paneque and Carmona. The corresponding potential ligand diphenylbis(pyrazolyl)borate (Bp^{Ph}) has been employed previously only in copper chemistry by the group of Tolman.[14] The published synthetic route described, starting from tetraphenylborate and 3-phenylpyrazole, yields the sodium salt $Na[Bp^{Ph}]$ contaminated by excessive amounts of 3-phenylpyrazole, which was separated manually. In addition, the yield was low (10%) so that we set out optimising the purification procedure. It turned out that lowering the reaction temperature and distillation at 105 °C yields a crude product that still contains two equivalents of 3-phenylpyrazole and recrystallisation from dichloromethane/pentane led to the crystalline sodium salt $Na(pz^{Ph})_2[Bp^{Ph}]$ (**1**^{pz}) in 77% yield (Scheme 1).

The molecular structure of **1**^{pz} is displayed in Figure 1. The sodium ion is coordinated in a distorted tetrahedral fashion by the Bp ligand as well as two pyrazole molecules. Since 3-phenylpyrazole rapidly tautomerises[15] it is not surprising to also find the 5-phenylpyrazole coordinated (see Figure 1). As expected,[13] the six-membered NaN_4B ring has a boat conformation. Compound **1**^{pz} seemed unsuitable as a starting material for the synthesis of iron complexes since it could be anticipated that the pyrazole molecules could coordinate to the iron as well. Their elimination was thus pursued and achieved by kugelrohr distillation at 160 °C in vacuo. This procedure leads to pure $Na[Bp^{Ph}]$ (**1**) in 71% yield (Scheme 1), which significantly improves the utility of this ligand. In addition, a full characterisation by



Scheme 1.

NMR spectroscopy became possible. By analogy with the preparation method developed for $Na[Bp^{Ph}]$, the new ligand precursors $Na[Bp^{tBu}]$ (**1***) and $Na[Bp^{Ph,Me}]$ (**1**′) (Scheme 2) were synthesised. The ligand Bp^{tBu} was anticipated to be suitable for studying the influence of the substituent varia-

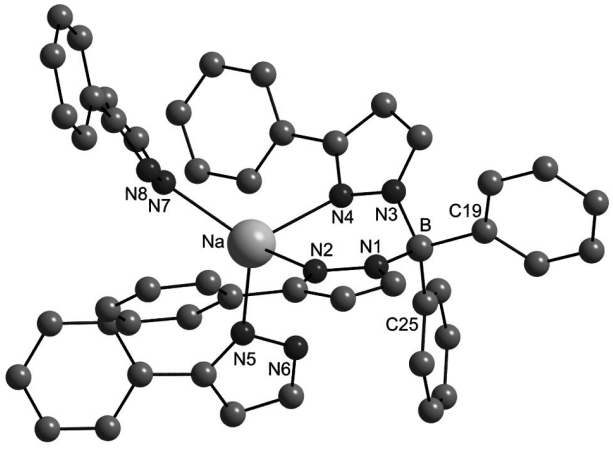
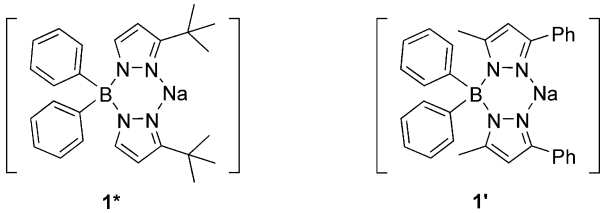


Figure 1. Molecular structure of $Na(pz^{Ph})_2(Bp^{Ph})$ (**1**^{pz}). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B–C19 1.630(3), B–C25 1.621(3), B–N3 1.570(2), B–N1 1.589(2), N1–N2 1.367(2), N3–N4 1.371(2), Na–N2 2.3809(17), Na–N4 2.3715(17), Na–N5 2.4242(19), Na–N7 2.4249(19); N1–B–N3 109.97(14), N3–B–C19 109.43(14), C19–B–C25 112.46(14), C25–B–N1 110.39(15), N1–B–C19 106.63(14), N3–B–C25 107.96(14), N2–Na–N4 81.43(5), N4–Na–N7 119.21(6), N7–Na–N5 120.71(6), N5–Na–N2 105.96(6), N2–Na–N7 117.38(6), N4–Na–N5 104.95(6).

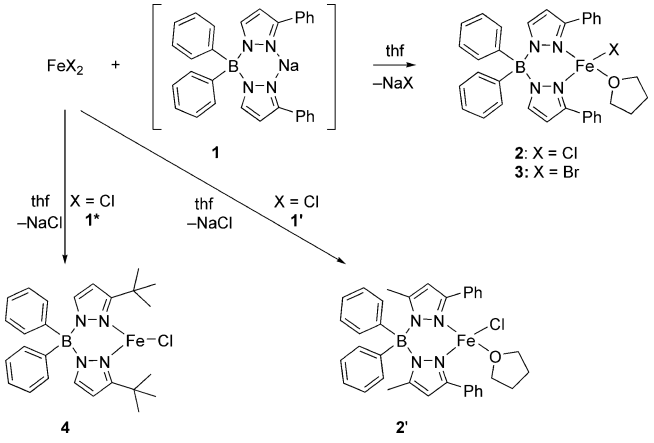


Scheme 2.

tion within the coordination pocket, and, in $Bp^{Ph,Me}$, the boron backbone is additionally protected by methyl residues.

Complex Synthesis

In complexation reactions it is essential to prevent any exposure to moisture. Even traces of water lead to protonation of the ligand (→ H[Bp]), since the water molecules become acidified by the iron starting materials. If, under rigorously inert conditions, a solution of **1** in thf is added to a solution of $FeCl_2$ in thf, appropriate workup leads to the iron complex [ClFe(thf)Bp^{Ph}] (**2**) in pure form as a white powder (Scheme 3).



Scheme 3.

Single crystals could be obtained by slow evaporation of the solvent from a corresponding thf solution and the result of an X-ray crystal structure analysis is shown in Figure 2.

The iron centre is located in a distorted tetrahedral coordination environment formed by the Bp ligand, one chlorido ligand as well as an additional thf solvent molecule, and the complex displays almost C_s symmetry. As described by Trofimenko for other metal complexes, the Bp ligand and the Fe centre form a six-membered chelate ring in a boat conformation.[13] Due to the smaller size of the Fe^{2+} ion in comparison with the Na^+ ion, the N–B–N angle is somewhat smaller in **2** [107.13(17)°] than in $\mathbf{1}^{pz}$ [109.97(14)°]. A μ_{eff} of 4.68 μ_B determined for **2** at room temperature indicates a high-spin configuration of the iron centre (the spin only value $\mu_{s.o.}$ amounts to 4.90 μ_B for four unpaired electrons). A Mössbauer spectrum of a powdered sample of **2** was recorded at 80 K (see Supporting Information, Figure S1). It consists of a doublet with δ = 0.98 mm s^{-1} and ΔE_Q = 3.69 mm s^{-1}. These values are similar to those obtained for other tetrahedral iron(II) complexes such as the thioacetamido (tha) complex $Fe(tha)_2Cl_2$ (δ = 1.09 mm s^{-1} and ΔE_Q = 3.28 mm s^{-1}) and the thiourea (thu) complex $Fe(thu)_2Cl_2$ (δ = 1.10 mm s^{-1} and ΔE_Q = 3.41 mm s^{-1}).[16] Compound **2** is very sensitive to air and moisture. Water leads to ligand protonation (vide supra), whereas contact with dioxygen results in an immediate brown colouration which indicates the formation of Fe^{III}. A

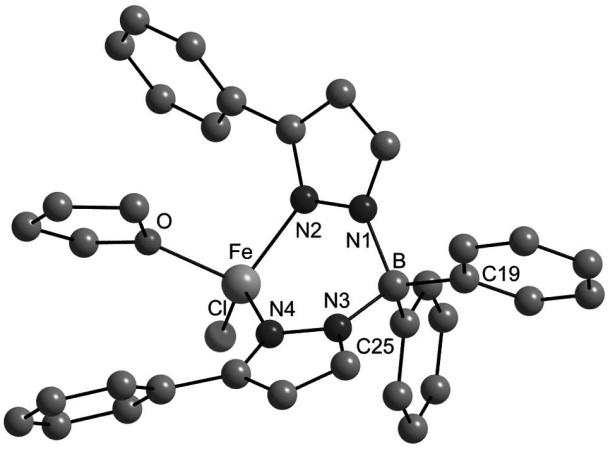


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C19–B 1.628(3), C25–B 1.611(3), B–N3 1.581(3), B–N1 1.598(3), Cl–Fe 2.2404(7), Fe–N2 2.0424(18), Fe–O 2.0604(17), Fe–N4 2.0606(18), N1–N2 1.368(2), N3–N4 1.374(3); N3–B–N1 107.13(17), N3–B–C25 109.66(17), N1–B–C25 108.75(17), N3–B–C19 108.25(18), N1–B–C19 108.00(17), C25–B–C19 114.78(18), N2–Fe–O 98.75(7), N2–Fe–N4 93.69(7), O–Fe–N4 98.28(7), N2–Fe–Cl1 126.99(6), O–Fe–Cl 107.18(5), N4–Fe–Cl 125.92(5).

derivative of **2**, [ClFe(thf)$Bp^{Ph,Me}$] (**2′**) was obtained when Na[$Bp^{Ph,Me}$] was employed instead of Na[Bp^{Ph}], and by analogy with the synthesis of **2**, a corresponding bromide complex, [BrFe(thf)Bp^{Ph}] (**3**), could be prepared in 17% yield starting from $FeBr_2$. Also for **3**, single-crystals could be obtained by evaporating the solvent from a thf solution so that an X-ray diffraction study could be performed. All bond lengths and angles (see Supporting Information, Figure S2) are very similar to those found in **2**.

A different result was obtained when Na[Bp^{tBu}] was employed in a reaction with $FeCl_2$. The complex [ClFeBp^{tBu}] (**4**) with a three-coordinate iron centre was formed. Its molecular structure is shown in Figure 3.

The metal centre is coordinated in a distorted trigonal planar fashion (the sum of the angles around the metal is 356°) by the Bp ligand and one chlorido ligand. The complex displays almost C_s symmetry. In contrast to three-coordinate β-diketiminato iron complexes, in which the metal centres are part of planar six-membered rings formed with the ligand,[17] the Fe-Bp chelate ring adopts a boat conformation in **4**. The Fe–Cl bond in **3** [2.2070(22) Å] is slightly longer than the corresponding bond in the β-diketiminato iron complex LFeCl [2.172(1) Å, L = 2,2,6,6-tetramethyl-3,5-bis(2,6-di-*iso*-propylphenylimido)heptane][17a] but, as expected, shorter than the Fe–Cl bond in **2** [2.2405(8) Å]. The reasons why the iron centre is only three-coordinate while **2** and **2′** contain an additional thf molecule are not clear. Certainly the *tert*-butyl residues are more bulky than phenyl residues (vide supra) but a thf ligand can still be accommodated at the iron centre within the structure of **4**. Presumably, after complexation of two negatively charged groups and one neutral donor function (i.e. Cl and Bp in **4**), a further neutral ligand is bound only weakly, so that it

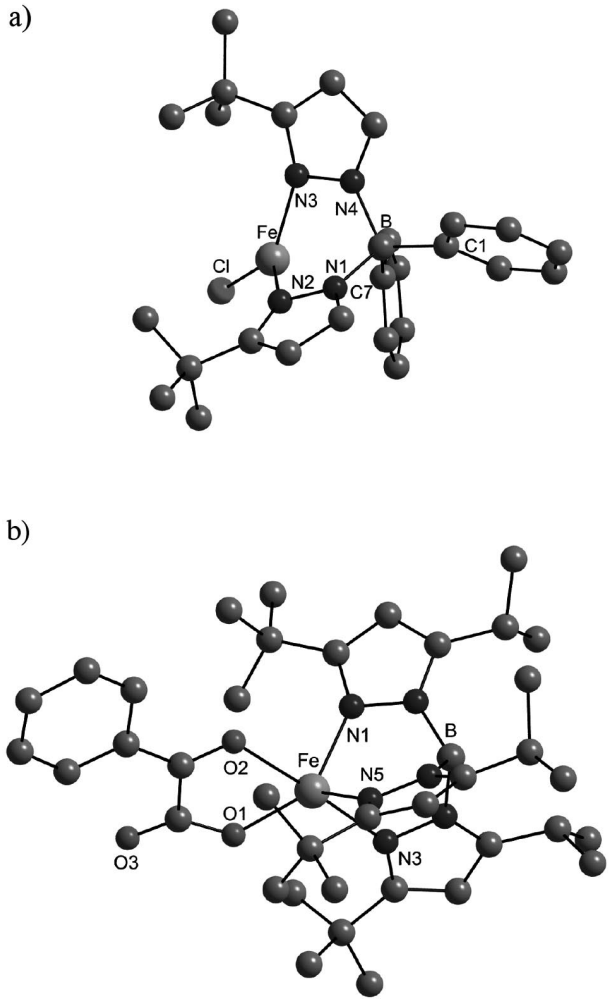


Figure 3. Molecular structure of **4** (a) and the structure of [Fe(Tp^{tBu,iPr})(BF)][3] (b) for comparison. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **4**: C7–B 1.640(11), C1–B 1.599(11), B–N4 1.576(10), B–N1 1.598(10), Cl–Fe 2.207(2), Fe–N2, 2.047(6), Fe–N3 2.075(6), N1–N2 1.369(8), N3–N4 1.377(8); N4–B–C1 112.2(6), N4–B–N1 107.2(5), C1–B–N1 109.1(6), N4–B–C7 107.9(6), C1–B–C7 114.6(6), N1–B–C7 105.4(6), N2–Fe–N3 92.0(2), N2–Fe–Cl 127.40(18), N3–Fe–Cl 136.11(17).

is absent in **4**. The fact that two further neutral ligands are formally bound in [Fe(Tp^{Ph,Ph})(BF)][3] (compare Figure 3) can be explained by the support of the chelating effect (BF as well as Tp), and it clearly shows that, in principle, there is sufficient space left for the coordination of further ligands.

Reactivity Studies

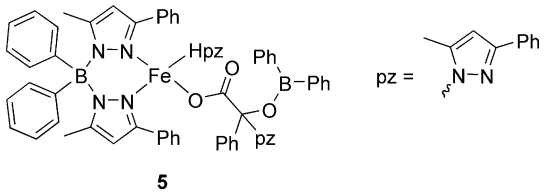
Complexes **2**–**4** all contain the Bp ligand, which can mimic the two histidines found in the active sites of many mononuclear nonheme iron enzymes. Furthermore, they all contain a halido ligand which is found beside the two histidine ligands within the halogenases.[7] These halido ligands also seemed valuable for a different purpose – they were anticipated to be replaceable by other negatively charged ligands for the simulation of further amino acid residues present in other nonheme iron enzymes (carboxylate, phenolate). Last, but not least, exogenous ligands (α-keto carboxylates, O_2 etc.) should be capable of replacing the halido and thf ligands, thereby finding sufficient room for further conversions. With this background, extensive reactivity tests were performed, which did not, however, lead to the anticipated results.

In an attempt to synthesise mimics of the $(His)_2$(carboxylate)Fe^{II} centre, we tried to substitute the chlorido ligands by carboxylate ligands. However, reactions of **2** and **3** with sodium trifluoroacetate or phenylacetate in thf did not lead to any colour change or the precipitation of NaCl, and there were no other indications of a successful conversion.

In order to test the potential of the complexes for the activation of dioxygen, perhaps in a dinuclear fashion by analogy with the soluble methanemonooxygenase, their reactivity in the presence of O_2 was investigated. Controlled treatment of the complexes with O_2 (also in the presence of the above-mentioned carboxylato ligands) led to a rapid colour change to brown, but the products eluded isolation and purification. On addition of substrates such as tetramethylethylene or 9,10-dihydroanthracene, no in situ conversion could be detected.

On treatment of **2**–**4** with benzoylformate [$^{-}O_2C$–C(=O)–Ph], a colour change to violet occurs, and this is characteristic for an iron(II)-to-α-keto-carboxylato charge transfer. This can also be observed in the native enzymes after binding of the α-keto acids.[18] However, we did not succeed in isolating these violet compounds from the product mixture, and the fact that all purification procedures led only to colourless compounds prompts the conclusion that the complexes of interest had only formed in small concentrations. We wanted to know the reasons for this behaviour, since the reactions are straightforward salt metatheses, and if these *can* proceed – as indicated by the colour change – the low yields seem peculiar. A possible answer is provided by a complex isolated after the reaction of **1′** with $Fe(OTf)_2(MeCN)_2$ and benzoylformate. Attempts to crystallise any product from this conversion led to the formation of small amounts of colourless crystals that could be investigated by single-crystal X-ray diffraction. The quality of the structure solution, however, was insufficient for a detailed discussion of bond lengths and angles. Nevertheless, the molecular structure in the solid crystalline state as shown in Figure 4 is beyond doubt, and Scheme 4 shows the formula derived for the product on the basis of the bond connectivities revealed by the structure.

The colour of the substance points to the +2 oxidation state for iron, and one positive charge is equalised by the Bp ligand, which coordinates in the usual fashion. The second positive charge is compensated for by the coordinated carboxylato function. This is connected to an sp^3 C atom that, before the reaction, belonged to the carbonyl function of the benzoylformate group, but subsequently also binds a pyrazole residue. The product can thus be derived from a formal addition of $Ph_2Bpz^{Ph,Me}$ across this C=O bond. Furthermore, 3,5-methylphenylpyrazole is coordinated to the iron ion. Even though this product was isolated only in



5

Scheme 4.

very small amounts, it is clear that the Bp ligand is sensitive with respect to B–N bond cleavages in the presence of nucleophiles. In order to examine whether this is intrinsically the case or whether precoordination by an iron ion is necessary, we have investigated the behaviour of **1** in the presence of NaBF in [D_8]thf. No decomposition could be detected, so we conclude that it requires coordination to the metal, especially since comparable deboronation reactions have been described earlier: finding that compound **5** contains a unit that can be derived from ligand **1′** by means of two B–N bond cleavages and formation of a B–O bond is reminiscent of proceedings observed earlier for TpMo complexes induced by addition of catechol, 2-aminobenzenethiole or isopropoxide.[19] In fact, several other hints to the sensitivity of the B–N bonds of the poly(pyrazolyl)borate ligand family can also be found in the literature,[20] and various attempts have been made to explain this. For instance, residual water in the solvents, nucleophilic groups or metal ions such as Ag^+ were claimed to be responsible for the degradations observed.[21] Furthermore, it has been suggested that the stability of the poly(pyrazolyl)borates is also influenced by the steric situation around the boron atom.[22] Bulky substituents at the boron centre (as here) or in the 3-position of the pyrazole units apparently even decrease the intrinsic stability of complexes in certain cases. While the complexes reported here are stable as such, the identification of **5** suggests an inherent sensitivity to carboxylate functions, and this could explain the inconsistent courses of the corresponding reactions described above. To confirm the hypothesis that the reactivity leading to **5** is not confined to this special case, the awareness of the peculiar

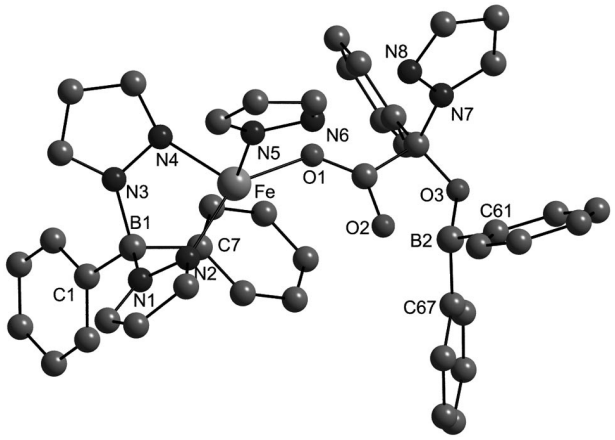


Figure 4. Molecular structure of **5**. The residues at the pyrazole units and all hydrogen atoms are omitted for clarity.

^-O_2C–CPh($pz^{Ph,Me}$)–$OBPh_2$ ligand found in **5** was used in a reexamination of the reaction of **2** with NaBF. Inside a glove-box, **2** was dissolved in acetonitrile, one equivalent of NaBF was added, and the reaction mixture was stirred for 6 h. Subsequently, the mixture was investigated by negative ESI-MS. The most intense peak had a mass (*m*/*e*) of 457.17463, which corresponds well to the exact mass calculated for ^-O_2C–CPh(pz^{Ph})–$OBPh_2$ (457.17234, correct isotopic splitting pattern), that is, **2** undergoes transformations similar to those that had yielded **5**. In accordance with this, a further intense peak could be assigned to $^-pz^{Ph}$.

Conclusions

Bis(pyrazolyl)borates (Bp) containing bulky substituents allow for the synthesis of iron(II) complexes, which, besides halido ligands, contain only one more thf ligand in the coordination sphere (if at all) that should be replaceable. The BpFe units nicely resemble $(His)_2Fe$ moieties found in many nonheme iron proteins, and as the residual coordination spheres offer more space for the binding of exogenous substrates than the corresponding ones in TpFe complexes, a comparatively higher reactivity with respect to the binding of benzoylformate, followed by reaction with O_2 and subsequent substrate oxidation was expected. All complexes proved to be highly reactive toward O_2, and a characteristic colour change on addition of benzoylformate also indicated a successful binding of this ligand, at least partly. However, the reactions do not proceed in a uniform way, and the identification of a side product combined with subsequent ESI-MS studies revealed the reason: after complexation by iron ions, the B–N bonds of the ligands are sensitive to attack by carboxylate functions so that the ligand becomes partially cleaved. Future research therefore has to address improving the stability of the ligand backbone for the envisaged purpose. Independently, despite the undesirable behaviour observed in contact with carboxylates, the low-coordinate BpFe complexes reported here seem attractive synthons for further syntheses that do not involve O-nucleophiles.

Experimental Section

General Remarks: Apart from the ligand synthesis, all manipulations were carried out in a glove-box or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AV 400 NMR spectrometer (^1H 400.13 MHz; ^{13}C 100.63 MHz) with DMSO as the solvent at 20 °C. The ^1H and ^{13}C NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuteriated solvent [D_6]DMSO δ_H = 2.50 ppm, δ_C = 39.43 ppm. Microanalyses were performed with a Leco CHNS-932 elemental analyser. ESI-MS-spectra were recorded with an Agilent Technologies 6210 Time-of-Flight LC/MS. Magnetic measurements were performed with an Alfa Magnetic Susceptibility Balance. Infrared (IR) spectra were recorded by using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR spectrometer. Mössbauer spectra were recorded with a ^{57}Co source in a Rh ma-

trix by using a Wissel Mössbauer spectrometer equipped with a Janis closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature. Simulations of the experimental data were performed with the Mfit program.[23] Solvents were dried with a Braun solvent purification system and degassed by vacuum-freezing cycles. Sodium benzoylformate (NaBF) was synthesised by deprotonation of benzoylformic acid with sodium hydroxide in methanol. 3-Phenylpyrazole,[24] 3-*tert*-butylpyrazole,[24] 5,3-methylphenylpyrazole[25] and $Fe(OTf)_2(MeCN)_2$[26] were synthesised as described earlier.

Synthesis of Na[Bp^{Ph}] (1): Sodium tetraphenylborate (5.78 g, 16.8 mmol) and 3-phenylpyrazole (21.90 g, 152 mmol) were stirred for 4.5 h at 195 °C. All benzene liberated during the reaction was continuously collected by distillation. Subsequently, excess pyrazole was removed at 105 °C under vacuum (5×10^{-3} mbar), and the resulting beige residue was dissolved in dichloromethane (100 mL). After concentration to 50 mL, a layer of pentane was added (150 mL), and the mixture was stored at –30 °C overnight. It was then warmed to room temp. with stirring. This procedure led to a white crystalline precipitate which was separated by filtration. Drying under vacuum at room temp. yielded 9.88 g (13.0 mmol, 77%) of **1^{pz}**. The residual two equivalents of pyrazole could be eliminated by kugelrohr distillation at 160 °C under vacuum (5×10^{-3} mbar), leading to 5.66 g (11.9 mmol, 71%) of **1** in the form of a white solid. m.p. 292 °C. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 6.44 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, PzH^4), 6.99–7.03 (m, 2 H, BPhH^4), 7.05–7.09 (m, 6 H, PzH^5 and BPhH^2), 7.18 (tt, J = 7.4, 1.4 Hz, 2 H, PzPhH^4), 7.28–7.34 (m, 8 H, PzPhH^2 and BPhH^3), 7.76 (dd, $^3J_{HH}$ = 8.2, 1.4 Hz, 4 H, PzPhH^3) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 99.4 (PzC^4), 124.1 (BPhC^4), 124.7 (PzPhC^3), 125.7 (BPhC^2), 125.8 (PzPhC^4), 128.2 (PzPhC^2), 134.0 (PzC^5), 135.6 (BPhC^3), 135.8 (PzPhC^1), 149.4 (PzC^3) ppm. IR (KBr): $\tilde{\nu}$ = 3132 (m), 3065 (m), 3052 (m), 3027 (m), 3002 (m), 1605 (m), 1489 (s), 1461 (vs), 1431 (vs), 1350 (vs), 1305 (w), 1267 (m), 1242 (m), 1234 (m), 1169 (s), 1159 (s), 1101 (m), 1072 (s), 1054 (m), 1027 (w), 1000 (m), 951 (m), 915 (w), 896 (m), 876 (m), 841 (s), 806 (m), 781 (s), 748 (vs), 731 (vs), 700 (vs), 664 (m), 641 (m), 615 (m), 517 (w), 450 (m) cm^{-1}. $C_{30}H_{24}BN_4Na$ (474.34): calcd. C 75.96, H 5.10, N 11.81; found C 74.97, H 5.37, N 11.95.

Synthesis of Na[Bp^{Ph,Me}] (1′): Sodium tetraphenylborate (2.13 g, 6.2 mmol) and 5,3-methylphenylpyrazole (9.80 g, 62 mmol) were stirred for 4 h at 200 °C. All benzene liberated during the reaction was continuously collected by distillation. Subsequently, excess pyrazole was removed at 160 °C under vacuum (5×10^{-3} mbar). Dichloromethane (40 mL) was then added to the residue at room temp., and the resulting white precipitate was separated by filtration. The white solid was washed with dichloromethane (10 mL) and dried under vacuum at room temp. to yield 1.98 g (63%) of **1′**. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 1.50 (s, 6 H, CH$_3$), 6.33 (s, 2 H, PzH^4), 6.88 (m, 2 H, PzPhH^4), 6.98 (m, 4 H, PzPhH^3), 7.13 (m, 2 H, BPhH^4), 7.29 (m, 8 H, BPhH^3 and PzPhH^2), 7.74 (m, 4 H, BPhH^2) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 12.3 (CH$_3$), 102.0 (PzC^4), 123.0 (PzPhC^4), 124.3 (BPhC^2), 125.1 (PzPhC^3), 125.3 (BPhC^4), 128.0 (BPhC^3), 134.1 (PzPhC^2), 136.1 (C$_{quart.}$), 143.9 (C$_{quart.}$), 146.8 (C$_{quart.}$) ppm. $C_{32}H_{28}BN_4Na$ (502.3): calcd. C 76.50, H 5.62, N 11.15; found C 76.51, H 5.93, N 11.02.

Synthesis of Na[Bp^{rBu}] (1*): Sodium tetraphenylborate (6.00 g, 17.5 mmol) and 3-*tert*-butylpyrazole (19.60 g, 157.8 mmol) were stirred for 4.5 h at 195 °C. All benzene liberated during the reaction was continuously collected by distillation. The resulting beige residue was dissolved in pentane (10 mL), and storing at –30 °C overnight led to a white precipitate which was separated by filtration. The residual two equivalents of pyrazole could be removed by kugelrohr distillation at 160 °C under vacuum. (5×10^{-3} mbar), leading to 3.97 g (52%) of **1*** in the form of a white solid. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 1.23 (s, 18 H, ^{t}Bu), 5.75 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, PzH^4), 6.63 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, PzH^5), 6.89–6.99 (m, 6 H, Ph), 7.34 (m, 4 H, Ph) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 31.2 (^{t}Bu), 97.1 (PzC^4), 123.5 (Ph), 125.3 (Ph), 133.6 (PzC^5), 134.0 (Ph), 159.3 (PzC^5) ppm. $C_{26}H_{32}BN_4Na$ (434.36): calcd. C 71.89, H 7.43, N 12.90; found C 70.96, H 7.28, N 12.35.

Synthesis of [ClFe(thf)Bp^{Ph}] (2): In a glove-box, **1** (666 mg, 1.40 mmol) in thf (10 mL) was added to $FeCl_2$ (178 mg, 1.40 mmol) in thf (10 mL). The mixture was stirred overnight, which led to a colourless solution. After removal of all volatiles, **2** was extracted with ethyl ether (50 mL) from the NaCl formed. The solution was concentrated to a volume of 30 mL, and storing overnight at –30 °C led to the precipitation of a white solid. This was separated by filtration, and drying under vacuum at room temp. led to **2** (80 mg, 0.13 mmol, 9%). Single crystals could be obtained by slow evaporation of the solvent from a thf solution. IR (KBr): $\tilde{\nu}$ = 3113 (w), 3067 (m), 3048 (m), 3004 (m), 2977 (m), 2897 (m), 2875 (w), 1488 (s), 1470 (s), 1432 (s), 1356 (s), 1264 (m), 1234 (m), 1187 (sh), 1167 (sh), 1154 (s), 1113 (m), 1080 (s), 1927 (m), 1009 (m), 954 (w), 918 (m), 874 (m), 835 (s), 802 (s), 789 (s), 763 (vs), 730 (vs), 701 (vs), 670 (m), 639 (m), 445 (w) cm^{-1}. $C_{34}H_{32}BClFeN_4O$ (614.75): calcd. C 66.43, H 5.25, N 9.11, Cl 5.77; found C 66.99, H 5.94, N 8.83, Cl 5.69. μ_{eff} = 4.68 μ_B. HR-ESI-TOF (positive, thf): m/z = 507.141 ([FeBp^{Ph}]$^+$ exact mass = 507.144).

Synthesis of [BrFe(thf)Bp^{Ph}] (3): Compound **1** (800 mg, 1.68 mmol) and $FeBr_2$ (363 mg, 1.68 mmol) were dissolved in thf (20 mL) and stirred for 2 h in a glove-box. After removal of all volatiles, **3** was extracted with ethyl ether (50 mL) from the NaBr formed. The solvent was removed in vacuo, and **3** (192 mg, 0.29 mmol, 17%) was obtained in the form of a white solid. Single crystals could be obtained by slow evaporation of the solvent from a thf solution. IR (KBr): $\tilde{\nu}$ = 3401 (w), 3110 (w), 3069 (w), 3047 (w), 3004 (vw), 2962 (w), 2923 (w), 2896 (vw), 2855 (m), 1951 (w), 1886 (w), 1559 (w), 1523 (w), 1486 (s), 1471 (s), 1443 (m), 1431 (s), 1352 (s), 1312 (m), 1262 (m), 1236 (m), 1153 (s), 1125 (m), 1079 (s), 1026 (m), 1009 (s), 986 (m), 954 (m), 921 (m), 917 (sh), 855 (m), 835 (s), 818 (sh), 801 (m), 788 (m), 762 (m), 746 (m), 729 (m), 702 (m), 687 (sh) 670 (w), 639 (w), 615 (vw) cm^{-1}. $C_{34}H_{32}BBrFeN_4O$ (659.20): calcd. C 61.95, H 4.89, N 8.50, Br 12.12; found C 61.03, H 5.27, N 8.31, Br 11.71.

Synthesis of [ClFe(thf)Bp^{Ph,Me}] (2′): Compound **1′** (502 mg, 1.00 mmol) and $FeCl_2$ (128 mg, 1.00 mmol) were suspended in thf (10 mL) and stirred for 4 h in a glove-box. After removal of all volatiles, **2′** was extracted with ethyl ether (30 mL) from the NaCl formed. The solvent was removed in vacuo, and **2′** was obtained in the form of a white solid (65 mg, 0.11 mmol, 11%). $C_{32}H_{28}BClFeN_4$ (570.70): calcd. C 67.35, H 4.95, N 9.82, Cl 6.21; found C 67.43, H 5.86, N 8.74, Cl 5.25. HR-ESI-TOF (positive, thf): m/z = 535.180 ([FeBp^{Ph,Me}]$^+$ exact mass = 535.176).

Synthesis of [ClFeBp^{rBu}] (4): Compound **1*** (434 mg, 1.00 mmol) and $FeCl_2$ (127 mg, 1.00 mmol) were dissolved in thf (10 mL) and stirred for 8 h in a glove-box. After removal of all volatiles, **4** was extracted with ethyl ether (30 mL) from the NaCl formed. The solvent was removed in vacuo, and **4** was obtained in the form of an off-white solid. Single crystals could be obtained by slow evaporation of the solvent from an ethyl ether solution. $C_{26}H_{32}BClFeN_4$ (502.67): calcd. C 62.12, H 6.42, N 11.15, Cl 7.05; found C 61.66, H 6.80, N 10.53, Cl 6.68.

Synthesis of 5: Compound **1′** (502 mg, 1.00 mmol) and $Fe(OTf)_2(MeCN)_2$ (436 mg, 1.00 mmol) were suspended in thf (10 mL) and, after stirring for 1.5 h, NaBF (157.3 mg, 0.9 mmol, 0.9 equiv.) was added, which led to a violet colouration of the solution. The solution was stirred for 2 h, and all volatiles were removed. Extraction with ethyl ether led to a violet solution from which colourless crystals of **5** were obtained by slow evaporation of the solvent.

Supporting Information (see footnote on the first page of this article): Mössbauer spectrum of **2** and crystal structure of **3**.

CCDC-679406, -679407, -679408, -679409, and -679410 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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