**N-Donor Competition in Iron Bis(chelate) Bis(pyrrozolyl)pyridinylmethane Complexes**

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**Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday**

We report on the synthesis and structural characterisation of the bis(chelate) bis(pyrrozolyl)pyridinylmethane iron(II) complexes 

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\text{[Fe\{HC(Pz)\textsubscript{2}(Py)\}\textsubscript{2}][CF\textsubscript{3}CO\textsubscript{2}]\textsubscript{2}}, \quad \text{[Fe\{HC(3-iPrPz)(5-iPrPz)(Py)\}\textsubscript{2}][CF\textsubscript{3}SO\textsubscript{3}]\textsubscript{2}}, \quad \text{and [Fe\{HC(3-iPrPz)(5-iPrPz)(Py)\}\textsubscript{2}][FeBr\textsubscript{4}][Br\cdot 2C\textsubscript{4}H\textsubscript{8}O]. During \}
\]

During the synthesis of the latter ones, an isomerisation of the ligand is observed: the pyrazolyl substituent formally moves from the 3 to the 5 position. Since the donor competition between pyrazolyl and pyridinyl moieties is important for the coordination properties, we also studied the donor properties by density functional theory and natural bond orbital analysis (NBO). As a result, the pyridinyl donor is generally weaker than the pyrazolyl donor, but the pyrazolyl donor is heavily influenced by the alkyl substitution pattern. To confirm the low-spin state of the complexes, magnetic susceptibility measurements have been performed.

**Key words:** Iron, Bis(pyrrozolyl)methane Complexes, X-Ray Crystallography, DFT, NBO

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**Introduction**

Bis(pyrrozolyl)methane ligands have emerged in coordination chemistry and especially in bioinorganic chemistry during the last years [1 – 8]. They offer a facial tridentate coordination environment for a multitude of metals [1 – 8]. Especially their combination with pyridinyl as a third donor function has been shown to be promising for the synthesis of tyrosinase models [9, 10]. Here, a donor competition between the pyridinyl and the pyrazolyl units can be observed. Regarding basicity, pyridine is three \( pK_a \) units more basic than pyrazole [11]. The relative donor strengths can be tuned through suited substitution as a subtle interplay of basicity and nucleophilicity [12, 13]. The pyrazolyl/pyridinyl donor competition is normally won by pyrazolyl, but small distortions of the metal’s coordinative preferences such as the Jahn–Teller distortion can change the picture [14].

Herein, we report on bis(chelate) iron complexes coordinated by bis(pyrrozolyl)methane ligands. Besides the unsubstituted ligand (2-pyridinyl)bis(pyrrozolyl)methane (HC(Pz)\(_2\)(Py)) which was originally reported by Canty et al. [15], we investigated the pyrazolyl-substituted ligand (2-pyridinyl)bis(3-isopropylpyrazolyl)methane HC(3-iPrPz)\(_2\)(Py) [16]. The substitution at the 3-position shall prevents the formation of bis(chelate) complexes and opens up coordination sites for catalytic reactivity. Remarkably, the systems sometimes try to avoid the steric pressure, and rearrangements of the substituents from 3- to 5-position occur when Lewis acids are present [17, 18]. This 3- to 5-isomerisation also happens when HC(3-iPrPz)\(_2\)(Py) reacts with iron(II) and again, bis(chelate) complexes are obtained. We investigated the donor competition
within these complexes by natural bond orbital analysis. Bis(chelate) iron complexes with N-donor ligands have found great attention in the field of spin crossover applications [19 – 23]. Small changes in substituents can influence the ligand field in such a way that the spin transition is facilitated at higher temperatures.

Results and Discussion

Synthesis and molecular structures of (2-pyridinyl)bis(pyrazolyl)methane iron complexes

Fe(II) tends to form octahedral bifacial complexes with (2-pyridinyl)bis(pyrazolyl)methane ligands [14]. Thus the reaction of Fe(CF$_3$CO$_2$)$_2$ and (2-pyridinyl)bis(pyrazolyl)methane (HC(Pz)$_2$(Py)) leads to the bis(chelate) complex [Fe(HC(Pz)$_2$(Py))$_2$] [CF$_3$CO$_2$]$_2$ (I[CF$_3$CO$_2$]$_2$) (Scheme 1), while the complexes [Fe(HC(3-iPrPz)(5-iPrPz)(Py))$_2$][CF$_3$SO$_3$]$_2$ (2[CF$_3$SO$_3$]$_2$) and [Fe(HC(3-iPrPz)(5-iPrPz)(Py))$_2$][FeBr$_4$]Br·2C$_4$H$_8$O (2[FeBr$_4$]Br) are obtained by reacting (2-pyridinyl)bis(3-iso-propylpyrazolyl)methane HC(3-iPrPz)$_2$(Py) with Fe(CF$_3$CO$_2$)$_2$ and FeBr$_2$, respectively (Scheme 2). During complex formation one iso-propylpyrazolyl unit undergoes isomerisation resulting in HC(3-iPrPz)(5-iPrPz)(Py) as the coordinating ligand. In all three complexes, the pyridinyl

Scheme 1. Synthesis of [Fe(HC(Pz)$_2$(Py))$_2$][CF$_3$CO$_2$]$_2$ (I[CF$_3$CO$_2$]$_2$).

moieties are trans-positioned as also found in related complexes [14].

The octahedral coordination of the central metal by two ligands is supported by HR-ESI-MS, showing the according mass peaks for the cationic complexes together with one corresponding counter ion. The molecular structures of all three complexes were determined by single-crystal X-ray diffraction. [Fe{HC(Pz)(Py)}]2[CF3CO2]2 (1) crystallises in the triclinic crystal system, space group P1 (Z = 1), as a symmetrical octahedral cationic complex with two counter ions in the outer coordination sphere (Fig. 1) and the iron(II) ion residing on a crystallographic centre of inversion.

The N-Fe-N angles varying from 87.4(1) to 88.9(1)° show that the octahedron is only slightly distorted. Both Fe–Npz distances are almost equal with 1.971(2) and 1.969(2) Å, but shorter than the Fe–Npy distance with 1.991(2) Å (Table 1).

The complexes [Fe{HC(3-PrPz)(5-PrPz)(Py)}]2[CF3SO3]2 (2) and [Fe{HC(3-PrPz)(5-PrPz)(Py)}]2[FeBr4]Br-2C5H8O (2[FeBr4]Br) crystallise in the same space group as 1[CF3CO2]2. Selected bond lengths and angles are summarised in Table 1. Crystallographic details are given in Table 2. During complex formation one PrPz moiety undergoes isomerisation from the 3- to the 5-position (Fig. 2). As a result, the pyrazolyl units differ with regard to their Fe–N bond lengths. The Fe–N5,4PrPz bonds (1.957(3) Å for 2[CF3SO3]2 and 1.957(5) Å for 2[FeBr4]Br) are shorter than the Fe–N3,4PrPz bonds (1.991(3) Å for 2[CF3SO3]2 and 1.998(5) Å for 2[FeBr4]Br).

**DFT calculations and NBO analyses**

In addition to the experiments, theoretical calculations were conducted, starting with a small structural benchmarking to determine a method that describes the experimental results correctly. At first complex 1[CF3CO2]2 was determined to be a low-spin complex by a SQUID measurement with a room temperature \(\chi_M T\) product of 0.61 cm\(^3\) K mol\(^{-1}\). In Fig. 3 the temperature dependence is given, proving that the spin state does not change significantly in the whole investigated temperature range (10 – 400 K).

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**Table 1.** Selected bond lengths (Å) and angles (deg) for [Fe{HC(Pz)(Py)}]2[CF3CO2]2 (1), [Fe{HC(3-PrPz)(5-PrPz)(Py)}]2[CF3SO3]2 (2) and [Fe{HC(3-PrPz)(5-PrPz)(py)}]2[FeBr4]Br-2C5H8O (2[FeBr4]Br).

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>1[CF3CO2]2</th>
<th>2[CF3SO3]2</th>
<th>2[FeBr4]Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Npy</td>
<td>1.991(2)</td>
<td>1.994(3)</td>
<td>1.981(5)</td>
</tr>
<tr>
<td>Fe–N5,4PrPz</td>
<td>1.969(2)(^a)</td>
<td>1.957(3)</td>
<td>1.957(5)</td>
</tr>
<tr>
<td>Fe–N3,4PrPz</td>
<td>1.971(2)(^a)</td>
<td>1.991(3)</td>
<td>1.998(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Npy–Fe–Npz</td>
<td>87.4(1)(^a)</td>
<td>89.2(1)</td>
<td>89.2(2)</td>
</tr>
<tr>
<td>Npy–Fe–N3,4PrPz</td>
<td>87.5(1)(^a)</td>
<td>87.3(1)</td>
<td>87.7(2)</td>
</tr>
<tr>
<td>N3,4PrPz–Fe–N5,4PrPz</td>
<td>88.9(1)(^a)</td>
<td>88.2(1)</td>
<td>88.1(2)</td>
</tr>
</tbody>
</table>

\(^a\): 5-PrPz and 3-PrPz are Pz.

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*Fig. 1 (colour online).* Molecular structure of the cationic complex [Fe{HC(Pz)(Py)}]2\(^{2+}\) (1) in crystals of 1[CF3CO2]2.

*Fig. 2 (colour online).* Molecular structure of [Fe{HC(3-PrPz)(5-PrPz)(Py)}]2\(^{2+}\) (2) in crystals of 2[CF3SO3]2 and 2[FeBr4]Br.
Table 2. Crystal structure data for 1[CF₃CO₂]₂, 2[CF₃SO₃]₂ and 2[FeBr₄]Br.

| Comp | Empirical formula | Crystal size, mm³ | Space group | a, Å | b, Å | c, Å | α, deg | β, deg | γ, deg | Rint | Refl. unique | Refl. collected | Dcalcd, g cm⁻³ | µ(Mo Kα), mm⁻¹ | F(000), e⁻¹ | hkl range |
|------|------------------|------------------|-------------|------|------|------|-------|-------|-------|------|----------------|----------------|----------------|----------------|----------------|--------------|-----------|
| 1    | C₃H₁₂F₂FeN₆O₄  | 0.16 × 0.12 × 0.10 | P T | 7.6068(3) | 10.8017(4) | 113.225(1) | 92.520(9) | 101.845(1) | 102.853(1) | 16 | 3605 | 15068 | 1.53 | 0.6 | 372 | ±9, ±14, ±14 |
| 2    | C₃H₁₄FeN₆O₄   | 0.08 × 0.05 × 0.03 | P T | 9.730(3) | 12.709(4) | 97.818(8) | 12.8265(10) | 98.472(9) | 92.520(9) | 138 | 3891 | 13068 | 1.45 | 0.5 | 504 | ±10, ±11, ±15 |
| 3    | C₃H₁₂FeBr₂     | 0.11 × 0.05 × 0.04 | P T | 11.9105(8) | 17.0875(13) | 89.996(2) | 87.385(2) | 86.834(2) | 2603.8(3) | 2 | 9162 | 45068 | 1.63 | 4.4 | 1278 | ±14, ±13, ±15, ±20 |

Table 3. Selected experimental and calculated bond lengths (Å) and angles (deg) for [Fe{HC(Pz)Py}₁₂][CF₃CO₂]₂ (1[CF₃CO₂]₂).

<table>
<thead>
<tr>
<th>Comp</th>
<th>BP86/ 6-31</th>
<th>BP86/ 6-311</th>
<th>B3LYP/ 6-31</th>
<th>B3LYP/ 6-311</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+g(d)</td>
<td>+g(d)</td>
<td>+g(d)</td>
<td>+g(d)</td>
</tr>
<tr>
<td>Fe-Np₄</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>Fe-Np₂</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>Fe-Np</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>Fe-Np₁</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Fig. 3. Plot of the χₙT product versus T for 1[CF₃CO₂]₂.

The selected functionals are B3LYP and BP86 in combination with the Pople basis sets 6-31+g(d) and 6-311+g(d). The results show a greater accordance of structural data between theory and experiment for the BP86 functional than for B3LYP (Table 3). Furthermore, the use of the triple-zeta basis 6-311+g(d) gives more accurate results than 6-31+g(d), where all bond lengths are too short. With regard to the calculated angles BP86 and B3LYP are showing good accordance with the results of the crystal structure. A variation of the basis set has almost no impact on the calculated angles.

As a result of this study, BP86/6-311+g(d) was applied in NBO3 and NBO6 second order perturba-
Table 4. Calculated NBO interaction energies \( E \) (kcal mol\(^{-1}\)) for \([\text{Fe}\{\text{HC}(\text{Pz})_2(\text{Py})\}_2]^{2+} \) (1) and for \([\text{Fe}\{\text{HC}(3\text{-iPrPz})(5\text{-iPrPz})(\text{Py})\}_2]^{2+} \) (2) (BP86/6-311+g(d)).

<table>
<thead>
<tr>
<th>1</th>
<th>( E ) (NBO3)</th>
<th>( E ) (NBO6)</th>
<th>2</th>
<th>( E ) (NBO3)</th>
<th>( E ) (NBO6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N_Pz} \rightarrow \text{Fe} )</td>
<td>198</td>
<td>141</td>
<td>( \text{N}_5\text{,iPrPz} \rightarrow \text{Fe} )</td>
<td>181</td>
<td>137</td>
</tr>
<tr>
<td>( \text{N_Py} \rightarrow \text{Fe} )</td>
<td>198</td>
<td>141</td>
<td>( \text{N}_{5,5\text{,iPrPz}} \rightarrow \text{Fe} )</td>
<td>163</td>
<td>124</td>
</tr>
</tbody>
</table>

Further NBO analysis of the model complex 3 (Table 5) reveals a dependence of the pyrazolyl donor ability on the position of functionalisation. If no isomerisation takes place, both pyrazolyl donors provide the same amount of energy with 150/122 kcal mol\(^{-1}\) (NBO3/NBO6) and are stronger donors than the pyridinyl unit with 141/119 kcal mol\(^{-1}\) (NBO3/NBO6). Because of steric hindrance the Fe–N bond lengths are larger in complex 3 than in 2, due to the repulsion of the iso-propyl groups, leading to lower energies.

Hence, the donor ability is dependent on the position of the iso-propyl group, raising the question of the impact of different alkyl groups on the donor ability. Therefore, the methyl (4) and tert-butyl (5) derivatives of 2 were built up by replacing the iso-propyl groups by the respective alkyls (Fig. 5).

At first, both complex structures were optimised, using BP86/6-311+g(d), and subsequently analysed by NBO second order perturbation theory (Table 6). A comparison of the Fe–N bond lengths reveals a continuous decrease in case of \( \text{N_Py} \) and \( \text{N}_{5,Pz} \), from methyl to tert-butyl, while the Fe–N\( _{3,Pz} \) distance increases (Table 6).
Fig. 5 (colour online). Calculated molecular structures of $[\text{Fe}\{\text{HC}(3\text{-MePz})(5\text{-MePz})(\text{Py})\}_2]^{2+}$ (4), $[\text{Fe}\{\text{HC}(3\text{-iPrPz})(5\text{-iPrPz})(\text{Py})\}_2]^{2+}$ (2) and $[\text{Fe}\{\text{HC}(3\text{-tBuPz})(5\text{-tBuPz})(\text{Py})\}_2]^{2+}$ (5).

Table 6. Calculated Fe–N bond lengths (Å) for 4, 2 and 5 (BP86/6-311+g(d)) with the respective alkyl rests in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>4 (methyl)</th>
<th>2 (iso-propyl)</th>
<th>5 (tert-butyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–N$_{\text{Py}}$</td>
<td>1.983</td>
<td>1.980</td>
<td>1.971</td>
</tr>
<tr>
<td>Fe–N$_{5\text{-Pz}}$</td>
<td>2.000</td>
<td>1.965</td>
<td>1.953</td>
</tr>
<tr>
<td>Fe–N$_{3\text{-Pz}}$</td>
<td>1.963</td>
<td>2.022</td>
<td>2.110</td>
</tr>
</tbody>
</table>

As shown in Table 7, there is an inverse correlation between bond length and donor ability (NBO3). Beside the decreasing Fe–N bond lengths for N$_{\text{Py}}$ and N$_{5\text{-Pz}}$, the stabilising energies diminish as well with 17 kcal mol$^{-1}$ for N$_{\text{Py}}$ and 21 kcal mol$^{-1}$ for N$_{5\text{-Pz}}$. In the case of N$_{3\text{-Pz}}$ an expected correlation of increasing bond length and decreasing stabilising interactions is obtained. The difference of 49 kcal mol$^{-1}$ between 4 and 5 shows the strong influence of alkyl derivatisation on the donor ability of 3-functionalised pyrazolyl units. Another result is the correlation between the increasing difference of Fe–N$_{3\text{-Pz}}$ and Fe–N$_{5\text{-Pz}}$ bond lengths from 0.037 (5) to 0.157 Å and the increase of the corresponding energy differences from 13 to 41 kcal mol$^{-1}$. By contrast, for NBO6 all pyridinyl units are of equal donor strength with 129 kcal mol$^{-1}$, and the decrease for N$_{5\text{-Pz}}$ and N$_{3\text{-Pz}}$ is still given but not as significant as for NBO3.

The prior optimisation of the molecular structures of 4 and 5 leads to a misleading conclusion concerning the substituent effects because of changes in the molecular structure due to substituent repulsion. Thus,
in a second approach the positions of the central metal and all coordinating nitrogen atoms were fixed to the values of cation 2. Optimisation of the structures of 4 and 5 followed by NBO analysis leads to a different picture of the influences of derivatisation on the metal-ligand interactions. In these complexes 5-iPrPz is always the strongest donor. For the methyl compound (4) the stabilising energy decreases for all three donor functionalities by 1 kcal mol\(^{-1}\) for \(\text{N}_5\-\text{Pr}\), 3 kcal mol\(^{-1}\) for \(\text{N}_5\-\text{Pz}\) and 8 kcal mol\(^{-1}\) for \(\text{N}_3\-\text{Pz}\) in comparison to the unconstrained complex (NBO3). By contrast, for compound 5 all stabilising energies increase by 5 kcal mol\(^{-1}\) for \(\text{N}_5\-\text{Pr}\), 4 kcal mol\(^{-1}\) for \(\text{N}_5\-\text{Pz}\) and 25 kcal mol\(^{-1}\) for \(\text{N}_3\-\text{Pz}\) (Table 8) toward the non-restricted complex (NBO3). These changes in Fe–N bond lengths diminish the influence of derivatisation on the donor ability as well as the differences between \(\text{N}_5\-\text{Pz}\) and \(\text{N}_3\-\text{Pz}\). The results with NBO6 also show a decrease in energy compared to the unconstrained complex, although a smaller one, for all three donor functionalities for 4 and 5. Overall, the \(\text{N}_5\-\text{Pr}\) remains the strongest donor in all three complexes, whereas the \(\text{N}_3\-\text{Pz}\) appears to be weaker than the \(\text{N}_5\-\text{Pr}\) donor. The NBO6 calculations demonstrate that there is indeed a small influence of the derivatisation on the donor abilities.

**Conclusion**

The structural characterisation of bis(chelate) iron bis(pyrazolyl)pyridinylmethane complexes has shown that second generation ligands are able to stabilise a bis(chelate) coordination after ligand rearrangement in form of a 3→5 isomerisation of the pyrazolyl substituent. The experimental results were complemented by DFT studies which reveal that in the unsubstituted complex cation 1, the donor ability of the pyrazolyl units is larger compared to that of the pyridinyl donors, but that the position of the substituents has a strong effect on the donor stabilisation energy. This is disclosed in the cation 2 as well as in the model cations 3→5 with varying position and nature of alkyl substituents. Here, a change of the position of the substituent can diminish the donor ability of the pyrazolyl unit to the value of the pyridinyl unit. This study allows new insights into the donor competition in transition metal bis(pyrazolyl)methane complexes.

**Experimental Section**

All reactions were carried out under a dry nitrogen atmosphere in a glove box. The solvents were degassed and dried following a standard procedure [24]. IR measurements were done with an FT/IR-460 Plus instrument from Jasco using an ATR unit. HR-ESI-MS experiments were performed on a Thermo Finigan LTQ FT Ultra Fourier Transform Ion cyclotron resonance mass spectrometer with an IonMax ion source (4 kV, 250 °C, MeCN). A sheathgas flow of 25 units and a sweepgas flow of 5 units were applied. Magnetic susceptibility data were collected using a MPMSXL-5 SQUID magnetometer under an applied field of 0.5 T over the temperature range 10 to 400 K in the settle mode. The samples were placed in gelatin capsules held within a plastic straw under argon protective atmosphere. The data were corrected for the diamagnetic contributions of the ligands by using tabulated Pascal’s constants.

All DFT calculations were conducted using Gaussian 09 (revision B.01) [25] and the implemented NBO3, as well as the stand-alone NBO6 [26] for all second-order perturbation theory calculations.

| \(\text{N}_5\-\text{Pz} \rightarrow \text{Fe}\) | 167 | 129 | 162 | 129 | 150 | 129 |
| \(\text{N}_3\-\text{Pz} \rightarrow \text{Fe}\) | 188 | 139 | 181 | 137 | 167 | 135 |
| \(\text{N}_3\-\text{Pr} \rightarrow \text{Fe}\) | 175 | 132 | 163 | 124 | 126 | 98  |

Table 7. Calculated NBO interaction energies \(E\) (kcal mol\(^{-1}\)) for \([\text{Fe}\{\text{HC}(3-\text{MePz})(5-\text{MePz})(\text{Py})\}]^2^+\) (4), \([\text{Fe}\{\text{HC}(3-i\text{PrPz})(5-i\text{PrPz})(\text{Py})\}]^2^+\) (2) and \([\text{Fe}\{\text{HC}(3-\text{tBuPz})(5-\text{tBuPz})(\text{Py})\}]^2^+\) (5) (BP86/6-311+g(d)).

| \(\text{N}_5\-\text{Pz} \rightarrow \text{Fe}\) | 166 | 129 | 162 | 129 | 155 | 130 |
| \(\text{N}_3\-\text{Pz} \rightarrow \text{Fe}\) | 185 | 137 | 180 | 137 | 171 | 135 |
| \(\text{N}_3\-\text{Pr} \rightarrow \text{Fe}\) | 195 | 132 | 163 | 124 | 150 | 122 |

Table 8. Calculated NBO interaction energies \(E\) (kcal mol\(^{-1}\)) for (4), (2) and (5) with fixed coordinates to the values of cation 2 for all coordinating N atoms and the Fe atom (BP86/6-311+g(d)).
[Fe(HC(Pz)2(Py)2)][CF3CO2]2, 1[CF3CO2]2

Iron(II) trifluoroacetate (77.3 mg) was dissolved in 2 mL CH2Cl2 and was added to a solution of HC(Pz)2(Py) (56.3 mg) in 2 mL CH2Cl2. The mixture was stored at room temperature. After 24 h the complex crystallised as orange blocks (90%). – IR (cm⁻¹): ν = 3135 νw, 2977 νw, 2870 w, 1782 νw, 1672 m (ν(C=O)), 1515 νw, 1478 w, 1436 w, 1407 m, 1368 νw, 1325 νw, 1258 m, 1249 m, 1190 s (ν(C=O)), 1139 νs (ν(C=O)), 1092 m, 1058 m, 1029 m, 993 m, 907 m, 875 m, 842 m, 799 m, 764 m, 731 m, 716 m, 691 m, 657 m. – HRMS (ESI, THF, m/z (%)): calcld.: 753.2440, found: 753.2442 (1) [Fe2(H3-PrPz)(5-PrPz)(Py)]+·1Br⁻, calcld.: 753.2440, found: 753.2442 (1) [Fe2(H3-PrPz)(5-PrPz)(Py)]+·2Br⁻.

Crystal structure determinations

The crystal data were collected with a Bruker D8 Venture with Bruker-AXS SMART [25] APEX CCD, using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction were performed with SAINT and SADABS [27]. The structure was solved by Direct Methods and conventional Fourier syntheses. All non-hydrogen atoms were refined anisotropically with full-matrix least-squares based on F^2 (XPREP [28]; SHELXL [29]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters Uiso(H) = 1.2Ueq(C) and 1.5Ueq(C methyl). All methyl groups were allowed to rotate but not to tip. In 1[CF3CO2]2 it was not possible to model the disordered solvent molecules (CH2Cl2) in an adequate manner, and the data set was treated with the SQUEEZER routine as implemented in PLATON [30, 31].

CCDC 1016618 (1[CF3CO2]2)_2, 1016619 (2[CF3SO3]2) and 1016620 (2[FeBr4]Br) 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.

Acknowledgement

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[27] SMART (version 5.62), SAINT (version 6.02), SHELXTL (version 6.10) and SADABS (version 2.03), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) 2002.


