

Supporting Information for:

Tris(5-methylpyrazolyl)methane: Synthesis and properties of its iron(II) complex

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Synthesis of tris(3-methylpyrazol-1-yl)methane regioisomer mixture. Following the general method of Reger et al.,¹ 3-methylpyrazole (1.64 g, 20 mmol), tetrabutylammonium bromide (0.32 g, 1.0 mmol), and sodium carbonate (12.7 g, 120 mmol) were heated together in a biphasic mixture of deionized water (40 mL) and chloroform (10 mL). The reaction mixture was allowed to gently reflux for ~72 hours under argon. After cooling and filtering, the organic layer was separated from the aqueous layer. The aqueous layer was extracted once with CH₂Cl₂ (100 mL), and the combined organic portions were washed twice with 100-mL portions of H₂O. The organic layers were combined and dried under vacuum to give a dark, brown oil. ¹H NMR analysis showed this to be mainly a mixture of all four regioisomers of the tpm derived from 3-methylpyrazole (Figure S1). The ¹H NMR spectrum of purified ligand **1** is shown in Figure S2 for comparison.

4 regioisomers from 3-methyl tpm

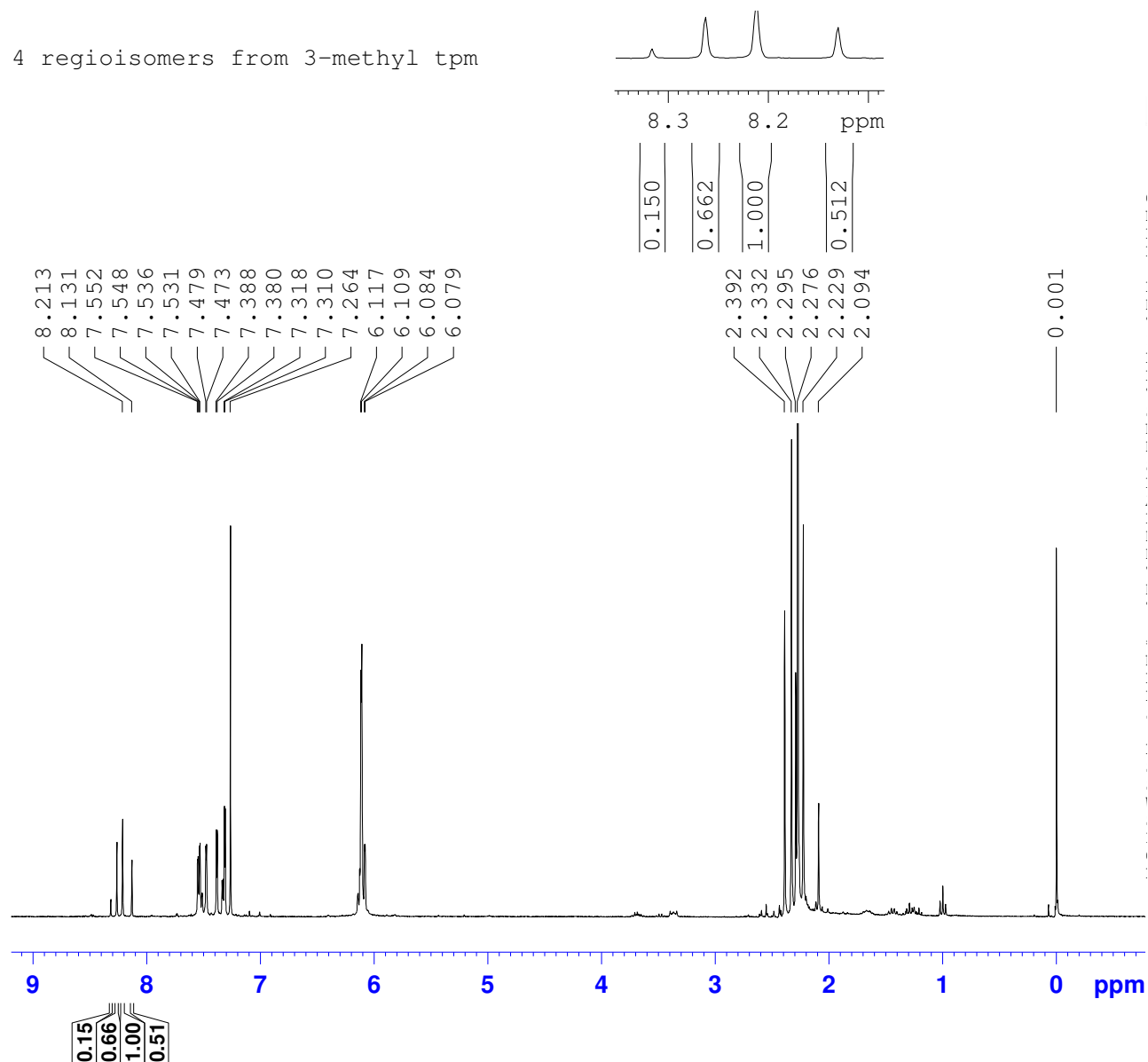


Figure S1. The NMR of the crude regioisomeric mixture. The inset in the upper right shows the methine peaks used to determine the product ratio. Compound **1** ($\delta = 8.32$) represents approximately 6% of the crude tpm mixture.

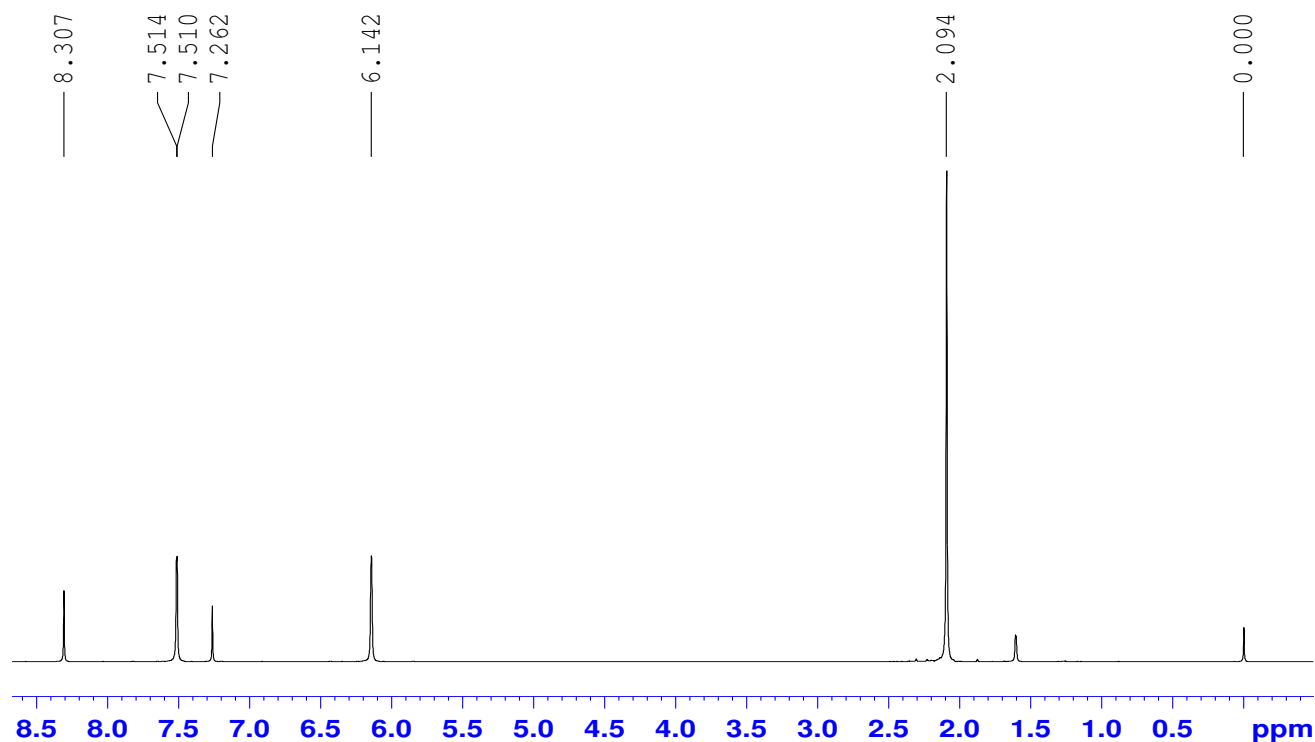


Figure S2. The NMR of tris(5-methylpyrazolyl)methane (**1**).

Deuteration study. A dry, 25-mL round-bottom flask was charged with 30 mg of tris(pyrazolyl)methane under argon. Dry THF (2.0 mL) was added via syringe and the solution was cooled to the desired temperature ($-78\text{ }^{\circ}\text{C}$ with dry ice/acetone; $-41\text{ }^{\circ}\text{C}$ with liquid nitrogen/acetonitrile; $-30\text{ }^{\circ}\text{C}$ in a laboratory freezer, $-10\text{ }^{\circ}\text{C}$ with ice/salt). The butyllithium (2.5 M in hexane) was added via syringe, and the mixture was stirred for time t_1 as described in Table S1. At the end of the time interval t_1 the reaction was quenched with d_4 -methanol (1.0 mL). The solvent was removed under reduced pressure, the residue was taken up in water and extracted with chloroform. The sample was dried with Na_2SO_4 , filtered, and evaporated to dryness. The ^1H NMR spectrum was acquired in CDCl_3 and the residual peaks from the H3, H5, and CH (methine) were integrated (Table S1). The results show that a temperature of $-30\text{ }^{\circ}\text{C}$ was required for complete removal of the H5 protons.

Table S1. The residual proton integration after treatment of tris(pyrazolyl)methane with *n*-butyllithium and quenching with *d*₄-methanol.

| T (°C) | butyllithium | t ₁ (min) | Ratio of ¹ H NMR integrals— H3:H5:CH(methine) |
|--------|--------------|----------------------|---|
| -78 | 6 equiv. | 20 | 31:23:1 |
| -78 | 6 equiv. | 30 | 57:17:1 |
| -78 | 6 equiv. | 60 | 45:11:1 |
| -41 | 6 equiv. | 20 | 15:1:1 |
| -41 | 6 equiv. | 30 | 17:2:1 |
| -41 | 6 equiv. | 60 | 25:1:1 |
| -30 | 6 equiv. | 20 | 87:3:1 |
| -30 | 6 equiv. | 30 | 74:2:1 |
| -30 | 6 equiv. | 60 | 71:2:1 |
| -10 | 6 equiv. | 20 | 36:1:1 |
| -10 | 6 equiv. | 30 | 62:2:1 |
| -10 | 6 equiv. | 60 | 72:2:1 |

Raman. To further characterize the Fe(II) complex **2**, a dispersive Raman spectrum of a powder sample was collected from 100–1500 cm⁻¹ on a Bruker Senterra Raman microscope using a 633 nm excitation laser operating at a power of 5.3 mW at the sample. A 50X ultra-long working distance objective was used to focus the excitation beam to an analysis spot size of approximately 1 μm directly on the sample, which was placed on a microscope slide. Spectral resolution was 3-5 cm⁻¹ across the spectral range analyzed. The resulting spectrum is shown in Figure S2.

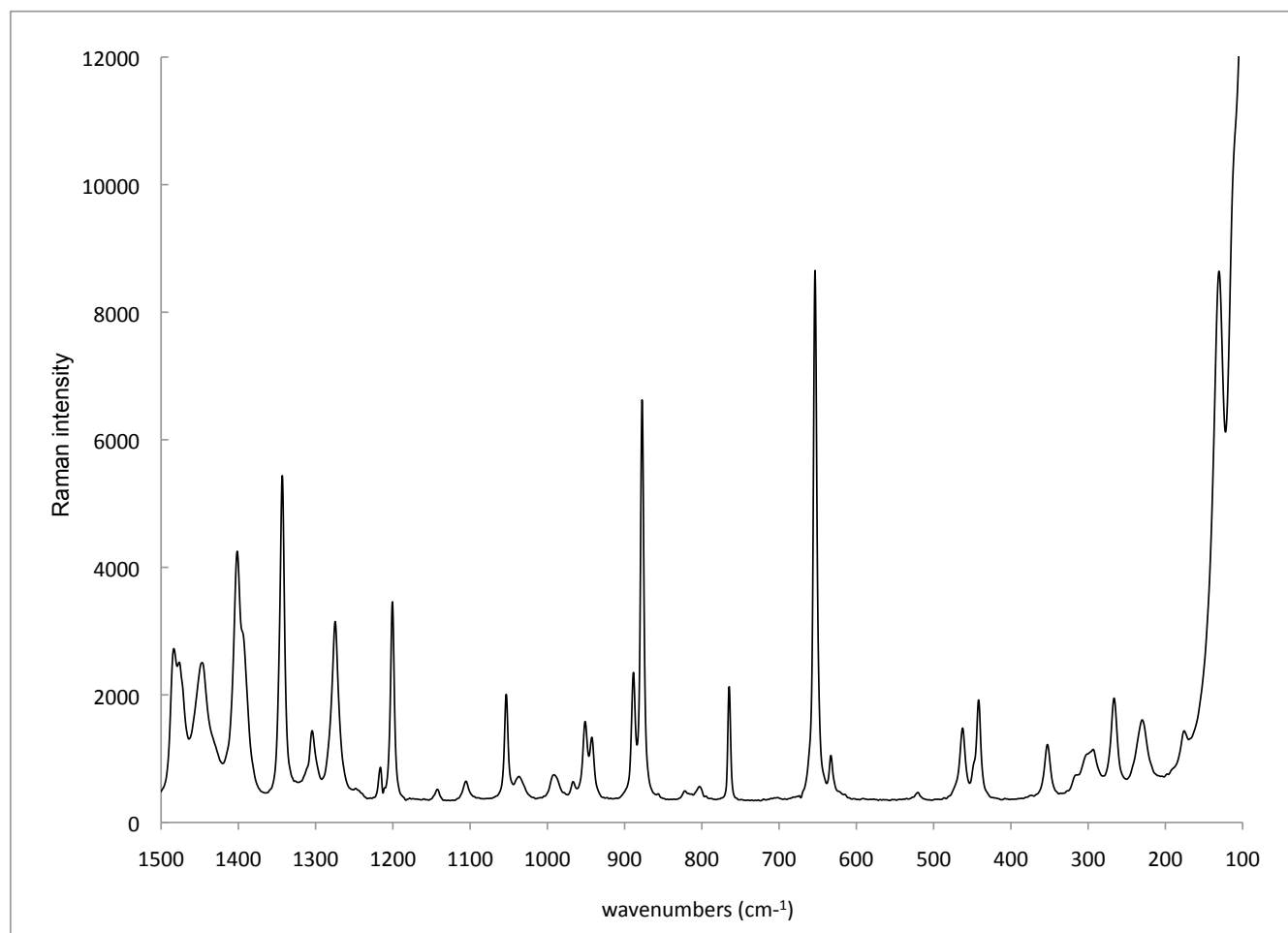


Figure S3. The Raman spectrum ($\lambda_{\text{ex}} = 633 \text{ nm}$) of complex **2**.

Octahedral distortion parameters. The octahedral distortion parameters, Σ and τ , have been calculated from the X-ray crystal structures of **2**, **2a**, and **2b** at each temperature examined. The parameter τ is simply the dihedral angle defined by the iron atom, N1 and N2 of the pyrazole, and the methine carbon of the tpm ligand. The parameter Σ is defined as follows:

$$\Sigma = \sum_{i=1}^{12} |90 - \alpha_i|$$

where α_i is each of the N—Fe—N bond angles in the pseudo-octahedral coordination sphere.

Table S2. Octahedral distortion parameters for Fe(II) complexes

| Compound | T (K) | Σ (°) | τ (°) |
|-----------|-------|--------------|------------------|
| 2 | 293 | 59.0 | 11.21 |
| | 100 | 34.7 | 10.54 |
| 2a | 300 | 58.6 | 9.73 |
| | 283 | 49.8 | 9.49 |
| | 263 | 42.1 | 9.32 |
| | 243 | 38.4 | 9.24 |
| | 173 | 36.0 | 9.62 |
| 2b | 293 | 27.2 | 0.62, 2.58, 2.73 |
| | 100 | 25.4 | 0.05, 2.44, 2.93 |

Analysis of Quadrupole Splitting. The low spin complex **2** at low temperature represents a relatively uncommon case of an Fe(II) compound with six identical ligands and non-zero quadrupole splitting (QS). According to the model of Bancroft,² the QS for ⁵⁷Fe can be expressed as:

$$QS = \frac{1}{2} e^2 q Q (1 + \eta^3 / 3)^{1/2}$$

where $q = V_{zz}/e$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and V are components of the electric field gradient tensor. In our case, the z -axis corresponds to the C_3 axis of the complex; from symmetry considerations it is clear that $V_{xx} = V_{yy}$ and $\eta = 0$; V_{zz} is proportional to $(3\cos^2\theta - 1)$. For an ideal octahedron, $\theta = \arccos(\sqrt{1/3}) \approx 54.7^\circ$ (the “magic angle”) and $V_{zz} = 0$. In the present case, the metal ion environment in **2** is not exactly octahedral, but is stretched out along C_3 axis (Figure S3). This results in smaller θ values (ca. 53°) and nonzero (and positive) V_{zz} . Therefore, quadrupole splitting is positive. This arrangement is in some way similar to that in Fephen_3^{2+} and Febipy_3^{2+} complexes; however, in these cases θ is always larger than the “magic angle” and QS is negative.³ Previously, positive QS values were observed for trigonal antiprism Fe(II) complexes, again with all six identical ligand atoms.³⁻⁵

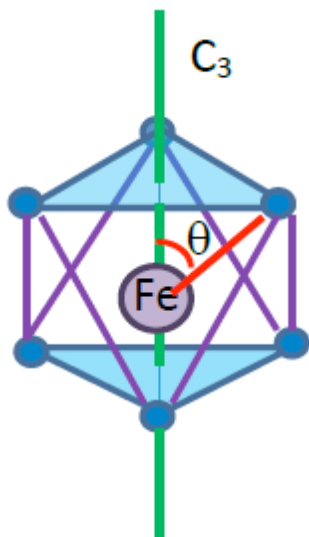


Figure S4. The coordination environment at iron for QS calculations

References

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