PROTON-DETECTED FAST-MAGIC-ANGLE SPINNING NMR OF PARAMAGNETIC INORGANIC SOLIDS

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1. Sample preparation

General Considerations

Unless stated otherwise, all reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purified and degassed by using standard procedures. All reagents were purchased from commercial suppliers and used without further purification. FT-IR spectra were recorded in the solid state by an ATR Golden Gate (Specac) on a PerkinElmer spectrum one spectrometer. Elemental analyses were determined at London Metropolitan University.

Synthesis of FeCl$_2$(THF)$_{1.5}$

Anhydrous FeCl$_2$ (5 g) was placed into a Soxhlet paper cartridge. A round bottom flask was charged with THF (150 mL) prior to be connected to the Soxhlet apparatus under argon. After 3 days of reflux a suspension of a white solid in a brown solution was obtained. The solid was filtered and washed with THF (30 mL) and dried under reduced pressure giving 6.77 g (73 %) of a white powder. Anal. found (calcd.) for FeCl$_2$•1.5C$_4$H$_8$O: C, 30.6 (30.7); H, 4.99 (5.15). IR (solid): ν(C-O-C THF): 875, 1023 cm$^{-1}$.

Synthesis of the N-(diisopropylphosphino)-N-methylpyridin-2-amine (py-NMe-PiPr$_2$)

The synthesis of the ligand was performed following the procedure described by Gambarotta’s group. 2-methylaminopyridine (1.0 mL, 9.80 mmol, 1.00 eq.) was dissolved in diethylether (30 mL) and the solution was cooled to -78 °C. n-BuLi (6.30 mL, 10.1 mmol, 1.03 eq.) was added dropwise to yield a light yellow solution which was then stirred for 1 h at -78 °C and for 2 h at ambient temperature. Diisopropylchlorophosphine (1.6 mL, 10.1 mmol, 1.03 eq.) was then added dropwise at 0 °C, and the reaction mixture was stirred overnight. The white suspension was transferred on an alumina column and washed with diethylether. The solvent was evaporated under reduced pressure until precipitation occurred. The product was filtered on paper disc and evaporated to dryness offering 1.90 g (86 %) of a colourless oil.

Scheme S1. Synthesis of the py-NMe-PiPr$_2$ ligand.

Synthesis of the FeCl$_2$[py-NMe-PiPr$_2$]$

The py-NMe-PiPr$_2$ ligand (0.674 g, 3.01 mmol, 1.05 eq.) and FeCl$_2$(THF)$_{1.5}$ (0.674 g, 2.87 mmol, 1.00 eq.) were suspended in toluene (20 mL) and stirred for two days at room temperature. A white solid precipitate was formed, which was subsequently filtered, washed twice with diethylether (30 mL) and dried under reduced pressure giving 0.917 g (91 %) of a white solid.
2. Sample characterization

The composition of the bulk was confirmed by elemental analysis. Anal. found (calcd.) for C₁₂H₂₂Cl₂FeNP: C, 41.05 (41.1), H, 6.12 (6.03), N, 7.82 (7.98).

Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a concentrated dichloromethane/toluene solution of complex 1. A crystal was selected and mounted on a nylon loop in perfluoroether oil on a Gemini kappa-geometry diffractometer (Rigaku Oxford Diffraction) equipped with an Atlas CCD detector and using Mo radiation (λ = 0.71073 Å). Intensities were collected at 150 K by means of the CrystAlisPro software. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrystAlisPro software. An analytical absorption correction was applied using the modeled faces of the crystal. The resulting set of hkl was used for structure solution and refinement. The structures were solved with the ShelXT structure solution program using the intrinsic phasing solution method and by using Olex2 as the graphical interface. The model was refined with version 2018/3 of ShelXL using full matrix least squares minimization on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

| Crystal data                  |                          |
|-------------------------------|--------------------------|
| Chemical formula              | C₁₂H₂₂Cl₂FeNP            |
| Mᵣ                           | 351.03                   |
| Crystal system, space group   | Monoclinic, P2₁/c        |
| Temperature (K)               | 293                      |
| a, b, c (Å)                   | 12.3959 (11), 23.352 (2), 11.4368 (10) |
| β (°)                         | 95.280 (7)               |
| V (Å³)                        | 3296.6 (5)               |
| Z                             | 8                        |
| Radiation type                | Mo Kα                    |
| μ (mm⁻¹)                      | 1.32                     |
| Crystal size (mm)             | 0.60 × 0.48 × 0.39       |

| Data collection               |                          |
|-------------------------------|--------------------------|
| Diffractometer                | Xcalibur, Atlas, Gemini ultra |
| Absorption correction         | Analytical               |
| Tmin, Tmax                    | 0.569, 0.706             |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 38663, 8368, 6789 |
| Rint                          | 0.090                    |
| (sin θ/λ)max (Å⁻¹)            | 0.692                    |

| Refinement                    |                          |
|-------------------------------|--------------------------|
| R[F² > 2σ(F²)], wR(F²), S     | 0.062, 0.170, 1.05       |
| No. of reflections            | 8368                     |
| No. of parameters             | 335                      |
| H-atom treatment              | riding                   |
| Δρmax, Δρmin (e Å⁻³)          | 1.11, −0.95              |

Table S1. Single-crystal X-ray diffraction experimental details
CCDC 2063303 contains 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/structures.

Figure S1. Thermal ellipsoid representation (at 50% probability) of complex 1. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P4-Fe1-N7 80.00(9); Cl2-Fe1-Cl3 121.11(5); N7-Fe1 2.075(3); P4-Fe1 2.419(11); Cl2-Fe1 2.247(12); Cl3-Fe1 2.228(13).

3. Solid-state NMR

Temperature calibration and gradients.

The sample temperature inside the 1.3 mm rotor was calibrated using the changes in the $^{207}\text{Pb}$ chemical shift of PbNO$_3$ , which depend linearly on the temperature with a slope of 0.753 ppm/°C, as published.\textsuperscript{7} The $^{207}\text{Pb}$ chemical shift was set to 0 ppm for a static sample, for which the thermocouple readout indicated 0 °C. At 60 kHz MAS, frictional heating caused a temperature increase of +52 °C with respect to the thermocouple readout. Temperature gradients within the sample were estimated to be ±5 °C from the width of the $^{207}\text{Pb}$ signal under the experimental conditions (60 kHz MAS, 260 K readout temperature).

$^{13}\text{C}$ direct-excitation spectra

For $^{13}\text{C}$ 1D spectra (Figure S4B) acquired in the 1.3 mm probe, the $\pi/2$ $^{13}\text{C}$ pulse lengths was 1.11 μs at 100 W, corresponding to RF field strengths of 226 kHz, at offsets of 400 ppm. Spectra were acquired with a rotor-synchronized double adiabatic echo experiment with a total double-echo time of 66.68 μs at 60 kHz MAS (four rotor periods). The adiabatic refocusing pulses were 33.33 μs long and swept through 5 MHz with a RF field strength of 50 W. No heteronucler $^1\text{H}$ dipolar decoupling was applied during the experiment.
Figure S2. Pulse diagrams for A) $^{13}$C-detected TEDOR and B) $^1$H-detected HSQC-TEDOR. Black and empty rectangles indicate π/2 and π pulses respectively. The pulse phase was cycled as follows, where 0, 1, 2 and 3 indicate a x, y, -x and -y pulse phase respectively, and $\{S\}^n$ indicates the repetition of a given phase sequence for $n$-times:

\[
\phi_1 = \{0 1 2 3 2 0 3 1 2 0 3 1 0 2 1 3\}; \quad \phi_2 = \{1 3 2 0 3 1 0 2 1 3\}; \quad \phi_3 = \{1 1 2 2 3 3 0 0\}; \quad \phi_4 = \{3 2 0 3 1 2 0 3 1 2 0 3 1 2 0 3\}; \quad \phi_5 = \{0 0 1 1 2 2 3 3 2 2 3 3 0 0 1 1\}; \quad \phi_6 = \{0 1 1 1 0 0 1 1\}; \quad \phi_{rec} = \{1 1 2 2 3 3 0 0\} \text{ and } B) \phi_1 = \{0 2\}; \quad \phi_2 = \{0 0 0 0 1 1 1 1\}; \quad \phi_3 = \{0 0 2 2\}; \quad \phi_4 = \{0 0 0 0 1 1 1 1\}; \quad \phi_5 = \{0 0 2 2\}; \quad \phi_6 = \{0 0 2 2\}; \quad \phi_7 = \{0 0 2 2\}; \quad \phi_{rec} = \{0 0 2 2\}.
\]

States-TPP1 are changed according the States-TPPI $f_1$ acquisition mode. Short 50 μs and 100 μs $z$-filters were used in TEDOR and HSQC-TEDOR, respectively.

Due to the requirement of a rotor-synchronized sampling of the indirect dimension ($f_1$), the spectral width in the indirect $^{13}$C dimension is limited by the MAS frequency. In the states-TPPI $f_1$ acquisition mode, this suppresses the spinning sidebands and removes line-shape distortions, but also produces folding of signals resonating outside this spectral window. The position of the folded resonances was identified by recording a second HSQC-TEDOR spectrum at 58 kHz MAS, i.e., with a 58 kHz $^{13}$C spectral widths in $f_1$. Between the two experiments, any signal folded $n$-times is shifted by $(n \times \DeltaSW)$ Hz in the indirect dimension, where $\DeltaSW = 2$ kHz is the difference in spectral width between the two experiments. Here, a shift of 2 kHz and 4 kHz for the two C3 and C10 signals appearing respectively at $\delta(1H) = 44$ and 265 ppm allowed to deduce the isotropic $\delta(13C)$ shifts of 570 and 1067 ppm, respectively, as illustrated in Figure S3.
Figure S3. Piecewise measurement of the HSQC-TEDOR spectrum of complex I at 60 kHz MAS (315 K, 500 MHz). Overlapped are two $^1$H-detected HSQC-TEDOR spectra acquired at 60 kHz MAS ($^{13}$C spectral width 60 kHz, red spectrum) and at 58 kHz MAS ($^{13}$C spectral width 58 kHz, green spectrum). The states-TPPI acquisition mode was used. In black, the reconstructed position of the C3 and C10 signals, unfolded from the red spectrum by 60 kHz and 120 kHz respectively. Asterisks (*) indicate $^1$H rotational sidebands. On the sides of the horizontal and vertical axes are reported the $^1$H aMAT isotropic projection and the directly-acquired $^{13}$C MAS spectrum, respectively.

Figure S4. Solid-state $^{13}$C NMR spectrum of I (312 K, 11.7 T, 60 kHz MAS). Rainbow-colored circles correspond to calculated shifts using different Hartree–Fock exchange admixtures to DFT functional used for hyperfine coupling calculations, ranging from 10 % (purple) to 40 % (red). For a complete list of predicted and experimental resonances, see Table S3.
Figure S5. Assessment of secondary effects on the calculation of $^1$H and $^{13}$C shifts. Calculated shifts are overlaid onto the unfolded HSQC-TEDOR spectrum (grey). (A) Effect of intermolecular PCS: shifts were calculated with (black) and without (red) intermolecular PCS. Calculations were performed on the X-ray geometry with optimized hydrogen atoms, at a temperature of 312 K. (B) Effect of temperature: shifts were calculated at 307 K (blue), 312 K (black), 317 K (red) on the X-ray geometry with optimized hydrogen atoms. Intermolecular PCS were included in the calculations. (C) Effect of geometry optimization: shifts were calculated on the X-ray geometry with optimized hydrogen atoms (black) and on an in-vacuo fully-optimized structure (red; the molecule becomes C$_s$ symmetric). Calculations were carried out at 312 K and did not include intermolecular PCS. (D) Effect of higher-order hyperfine coupling terms (“A2 terms”): shifts were calculated without (black) and with (red) the “A2 terms”. Calculations were carried out on the X-ray geometry with optimized hydrogen atoms at a temperature of 312 K, and intermolecular PCS were not included.

4. Quantum chemistry calculations

| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| Fe      | 5.9244853    | 14.0415541   | 8.0250597    |
| Cl      | 4.3837298    | 15.5519606   | 7.3982459    |
| Cl      | 5.3781045    | 11.9064807   | 8.3493007    |
| P       | 7.5458189    | 14.9371028   | 9.5810303    |
| N       | 8.8541175    | 15.1547427   | 8.5171806    |
| C       | 8.7155086    | 14.8322518   | 7.1725430    |
| N       | 7.5656349    | 14.2267350   | 6.7688091    |
| C       | 7.4546869    | 13.8213441   | 5.4686505    |
| C       | 8.4214566    | 14.0088611   | 4.5425727    |
| C       | 9.5797513    | 14.6930739   | 4.9497276    |
| C       | 9.7208363    | 15.1110748   | 6.2612912    |
| H       | 10.6225242   | 15.6388603   | 6.5661951    |
| H       | 10.3764774   | 14.9008546   | 4.2314633    |
| H       | 8.2933997    | 13.6617791   | 3.5172398    |
Table S2. Cartesian coordinates of the XRD structure of complex 1 with hydrogen atoms optimized with DFT (PBE0-D3(BJ) / def2-SVP, Fe: def2-TZVP).

5. Summary of experimental and calculated shifts

Table S3. Experimental NMR shift in solid state (δKss) as well as calculated values (δK) obtained with Hartree–Fock exchange admixture (HFX) for hyperfine coupling calculation ranging from 10 to 40%. Intermolecular PCS are included in all calculations. All values are listed in ppm.

| HFX | 10% | 15% | 20% | 25% | 30% | 35% | 40% |
|-----|-----|-----|-----|-----|-----|-----|-----|
| K   | δK  | δKss |     |     |     |     |     |
|-----|-----|------|-----|-----|-----|-----|-----|
| H2  | 162.9 | 145.9 | 130.7 | 117.0 | 104.8 | 94.6 | 82.6 | N/A  |
| H3  | 57.3 | 55.4 | 54.3 | 53.7 | 53.7 | 53.4 | 55.7 | 44 |
| H4  | -77.3 | -75.8 | -75.0 | -74.9 | -75.3 | -75.2 | -77.8 | N/A  |
| H5  | 93.7 | 88.5 | 84.5 | 81.5 | 79.2 | 76.9 | 77.8 | 63 |
| H8  | 17.6 | 16.0 | 14.8 | 13.8 | 13.0 | 12.3 | 12.0 | 11 |
| H10 | 346.3 | 318.4 | 294.2 | 273.3 | 255.1 | 239.3 | 225.7 | N/A  |
| H11 | -4.0 | -2.9 | -2.0 | -1.2 | -0.5 | 0.1 | 0.6 | 6  |
| H12 | -2.6 | -2.2 | -2.0 | -1.7 | -1.5 | -1.4 | -1.2 | -6  |
| H10' | 365.1 | 335.3 | 309.4 | 286.8 | 267.3 | 250.3 | 235.8 | 264.6 |
| H11' | -3.6 | -2.3 | -1.2 | -0.3 | 0.5 | 1.2 | 1.8 | 6  |
| H12' | -0.2 | -0.5 | -0.6 | -0.7 | -0.8 | -0.8 | -0.9 | -6  |

| K   | δK  | δKss |     |     |     |     |     |
|-----|-----|------|-----|-----|-----|-----|-----|
| C2  | -420 | -393 | -363 | -329 | -293 | -262 | -219 | N/A  |
| C3  | 554 | 504 | 458 | 414 | 372 | 338 | 286 | 570 |
| C4  | 455 | 457 | 462 | 470 | 480 | 487 | 514 | 257 |
| C5  | 256 | 233 | 208 | 182 | 155 | 132 | 92 | 220 |
| C6  | -159 | -149 | -132 | -110 | -87 | -67 | -27 | -157 |
| C8  | 41 | 66 | 83 | 92 | 98 | 100 | 98 | 210 |
| C10 | 1309 | 1222 | 1148 | 1084 | 1027 | 977 | 934 | 1067 |
| C11 | -116 | -107 | -98 | -89 | -81 | -73 | -67 | 30 |
| C12 | 14 | 33 | 47 | 57 | 64 | 68 | 73 | 119  |
| C10' | 1222 | 1158 | 1101 | 1048 | 1000 | 955 | 920 | 1019  |
| C11' | -137 | -131 | -124 | -116 | -108 | -100 | -93 | -14  |
| C12' | 45 | 61 | 73 | 81 | 86 | 90 | 93 | 119  |

* Signals were not observed due to a fast inter/intramolecular paramagnetic-induced relaxation. * Signals from near-equivalent atoms of iso-propyl groups were not resolved. * Near-equivalent atoms of iso-propyl groups experiencing non-symmetry due to crystal packing were resolved in a 13C MAS experiment.
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