SUPPORTING INFORMATION

DOI: 10.1002/ejic.201500873

Title: The First Coordination Polymers Based on 1,3-Diphosphaferrocenes and 1,1’,2,3’,4-Pentaphosphaferrocenes

Author(s): Claudia Heindl, Sabine Reisinger, Christoph Schwarzmaier, Lena Rummel, Alexander V. Virovets, Eugenia V. Peresypkina, Manfred Scheer*
X-ray structural details

List of structurally characterized compounds:

2: $[\text{Cp}^*\text{Fe}(\eta^5:\text{P}_2\text{C}_3\text{iPr}_3)]$
4: $[(\eta^5:\text{P}_2\text{C}_3\text{iPr}_3)_2\text{Fe}]$
5, 5', 5'': $[(\eta^5:\text{P}_2\text{C}_3\text{iPr}_3)_2\text{Fe}(\eta^5:\text{P}_2\text{C}_3\text{iPr}_3)]$
2-Br: $[[\text{Cp}^*\text{Fe}(\mu_3,\eta^{5:1:1}\text{P}_2\text{C}_3\text{iPr}_3)]\text{Cu}_2(\mu-\text{Br})_2(\text{CH}_3\text{CN})]_n 0.75(\text{CH}_3\text{CN})$
2-I: $[[\text{Cp}^*\text{Fe}(\mu_3,\eta^{5:1:1}\text{P}_2\text{C}_3\text{iPr}_3)]\text{Cu}_2(\mu-\text{I})_2(\text{CH}_3\text{CN})_{0.5}]_n 0.5(\text{CH}_3\text{CN})$
3-Cl; 3-Cl': $[[\text{Cp}^*\text{Fe}(\mu_4,\eta^{5:1:1:1}\text{P}_2\text{C}_3\text{iPr}_3)]\text{Cu}_2(\mu-\text{Cl})_2]_n$
3-Br: $[[\text{Cp}^*\text{Fe}(\mu_4,\eta^{5:1:1:1}\text{P}_2\text{C}_3\text{iPr}_3)]\text{Cu}_2(\mu-\text{Br})_2]_n 0.15\text{C}_7\text{H}_8$
5-Br: $[[((\mu_3,\eta^{5:1:1}\text{P}_2\text{C}_3\text{iPr}_3)\text{Fe}(\mu,\eta^{5:1}\text{P}_2\text{C}_3\text{iPr}_3))\text{Cu}_3(\mu-\text{Br}(\mu_3-\text{Br})(\mu_4-\text{Br})]_n 0.5\text{C}_7\text{H}_8$
5-I: $[[((\mu,\eta^{5:1}\text{P}_2\text{C}_3\text{iPr}_3)\text{Fe}(\mu,\eta^{5:1}\text{P}_2\text{C}_3\text{iPr}_3))\text{Cu}_3(\mu-3-\text{I})_2]_n$

The crystals were taken from a Schlenk flask under a stream of argon and immediately covered with mineral oil or perfluorinated Fomblin® mineral oil to prevent both decomposition and a loss of solvent. The quickly chosen single crystals covered by a drop of the oil were taken to the pre-centered goniometer head with CryoMount® and directly attached to the diffractometer into a stream of cold nitrogen.

All structures were solved by direct methods with SHELX97. The structures were refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using SHELXL97 or the multiprocessor and variable memory version SHELXL2013. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined riding on pivot atoms.

Crystals of 2-I and 5 proved to be inversion twins crystallizing in chiral $P2_1_2_1_1$ and $P2_1$ space groups, respectively. The corresponding twin batches were refined as 0.593(3)/0.407(3) and 0.888(5)/0.112(5).
The pentaphosphaferrocene crystallized in three monoclinic polymorphic modifications as 5, 5' and 5''. A pseudosymmetry was detected by PLATON in the crystal structure of 4 as an inversion center. Taking into account that the structure is triclinic (P1) an additional symmetry element can end up only in a smaller unit cell. Indexation of the diffraction pattern gives the reported unit cell, but analysis of the spatial distribution of the strongest reflections shows a three times smaller possible subcell, and \( a = 8.659, b = 8.880, c = 9.644, \alpha = 79.29, \beta = 78.02, \gamma = 61.70 \). The transformation matrix from the subcell to the large unit cell is \((0 1 -1, 1 -1 -1, -1 0 -1)\). Our attempt to solve and refine the structure in the subcell returned half of the molecule as an independent part and \( R_1 = 0.037 \), however with flattened a.d.p. ellipsoids of the carbon atoms belonging to the methyl groups. The comparison of the a.d.p. ellipsoids in two independent molecules in the large unit cell with those in the subcell allows us to conclude that the superstructural effects originate from a conformational flexibility of the \( i\text{-Pr} \) groups.

A \( B \)-centering was detected by PLATON in the crystal structure of 2. However, the \( I/\sigma \) for the reflections that violate this \( B \)-centering is still high, 14.5, compared to mean \( I/\sigma = 32.8 \). Figure S1 shows the reason for this pseudosymmetry; two independent molecules that could be related by \( b \) translation would coincide except for two \( i\text{-Pr} \) groups.

In 2-I, one of the \( i\text{-Pr} \) groups of the \( P_2C_3 \) ring is disordered with a relative weight refined to 0.6/0.4 over two close positions, whose atoms were not possible to refine anisotropically for this reason. In both structures, 3-Br and 5-Br, solvated toluene molecules are disordered in a similar fashion over an inversion center so that the Me group of one position overlaps with the 4-carbon of a benzyl ring of the other. The carbon atoms of the toluene were refined in an isotropic approximation. The atoms of the coinciding positions were refined with equated displacement parameters. Since overall molecular occupancy is 0.3 for 3-Br, the geometry of the molecule was refined with geometrical restraints. In 2-Br one of the solvated MeCN molecule has a molecular occupancy of 0.5 and is disordered over the center of symmetry. It was refined in an isotropic approximation.

The crystals of 5-I were systematically twinned as stack of plates. For this reason a very thin crystal was chosen for the measurement. Nevertheless, the twinning could not be completely avoided that resulted in high \( K \) and \( R_{int} \) values. The number of carbon atoms was refined with restrained anisotropic displacement parameters.

Crystallographic data and details of the diffraction experiments are given in Table S1 - Table S3. CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for all compounds are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-1415107 - CCDC-1415118, respectively. All figures in the Supporting Information are created with Olex Software.\(^2\)
Table S1. Experimental details for compounds 2, 4, 5 and 5'.

|       | 2               | 4               | 5               | 5'              |
|-------|-----------------|-----------------|-----------------|-----------------|
| CCDC Codes | CCDC-1415107 | CCDC-1415108 | CCDC-1415109 | CCDC-1415110 |
| Chemical formula | C_22H_34FeP_2 | C_24H_42FeP_4 | C_20H_35FeP_5 | C_20H_35FeP_5 |
| M_r | 418.30 | 510.31 | 486.18 | 486.18 |
| Crystal system, space group | Monoclinic, P2_1/c | Triclinic, P1 | Monoclinic, P2_1 | Monoclinic, P2_1/n |
| Temperature (K) | 123(2) | 123(1) | 123(1) | 123(2) |
| a, b, c (Å) | 9.1532 (2), 33.9928 (5), 14.0171 (2) | 11.8344 (3), 13.0807 (4), 14.2363 (4) | 9.6056 (1), 16.9567 (2), 14.3763 (2) | 9.5449 (1), 15.9135 (2), 15.1917 (1) |
| α, β, γ (°) | 90.330 (1) | 67.789 (3), 69.866 (3), 77.591 (2) | 92.825 (1) | 94.664 (1) |
| V (Å^3) | 4361.25 (13) | 1906.47 (11) | 2338.76 (5) | 2299.87 (4) |
| Z | 8 | 3 | 4 | 4 |
| F(000) | 1792 | 816 | 1024 | 1024 |
| Radiation type | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| Crystal colour and shape | Orange plate | Red-brown block | Green block | Green plate |
| Crystal size (mm) | 0.47 × 0.24 × 0.06 | 0.29 × 0.21 × 0.19 | 0.19 × 0.09 × 0.08 | 0.22 × 0.14 × 0.04 |
| Diffractometer | SuperNova, Single source at offset, Atlas diffractometer | Xcalibur, Ruby, Gemini ultra diffractometer | Xcalibur, Ruby, Gemini ultra diffractometer | SuperNova, TitanS2 diffractometer |
| Absorption correction | Gaussian | Analytical | Analytical | Gaussian |
| T_{min} T_{max} | 0.226, 0.677 | 0.296, 0.430 | 0.412, 0.655 | 0.317, 0.732 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 44567, 8422, 7502 | 23628, 6639, 5013 | 14958, 7064, 6636 | 24371, 4626, 4258 |
| R_{int} | 0.047 | 0.029 | 0.027 | 0.054 |
| (sin θ/λ)_{max} (Å^{-1}) | 0.624 | 0.595 | 0.595 | 0.624 |
| Range of h, k, l | h = -10→11, k = -42→41, l = -17→17 | h = -14→14, k = -15→15, l = -16→16 | h = -9→11, k = -19→20, l = -17→17 | h = -11→11, k = -18→19, l = -18→18 |
| Refinement | | | | |
| R[F^2 > 2σ(F^2)], wR(F^2), S | 0.037, 0.106, 1.04 | 0.030, 0.079, 0.90 | 0.036, 0.097, 1.11 | 0.026, 0.069, 0.99 |
| No. of reflections | 8422 | 6639 | 7064 | 4626 |
| No. of parameters | 473 | 394 | 470 | 245 |
| No. of restraints | 0 | 0 | 1 | 0 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δρ_{max}, Δρ_{min} (e Å^{-3}) | 0.71, -0.47 | 0.44, -0.38 | 0.86, -0.33 | 0.49, -0.45 |

Computer programs: CrysAlis PRO, Agilent Technologies, SHELXL97 (Sheldrick, 1997), SHELXL2013 (Sheldrick, 2013), PLATON (Spek, 1990), PLATON (Spek, 2003).
Table S2. Experimental details for compounds 5’, 2-Br, 2-I and 3-Cl.

|                  | 5’   | 2-Br | 2-I  | 3-Cl  |
|------------------|------|------|------|-------|
| CCDC Codes       | CCDC-1415111 | CCDC-1415112 | CCDC-1415113 | CCDC-1415115 |
| Chemical formula | C₆H₅FeP₃ | C₆H₅Br₃Fe₃(P₂-0.75(CH₂CN)) | C₆H₅Br₃Fe₃(P₂-0.75(CH₂CN)) | C₆H₅Cl₃Fe₃(P₂) |
| Mᵣ              | 486.18 | 777.04 | 840.23 | 592.15 |
| Crystal system, space group | Monoclinic, P2₁/n | Monoclinic, C2/c | Orthorhombic, P2₁2₁2₁ | Orthorhombic, Pbca |
| Temperature (K)  | 126(3) | 123(2) | 123(1) | 123(2) |
| a, b, c (Å)      | 13.6464(4), 12.1784(2), 28.7527(8) | 25.4093(5), 19.3055(2), 15.7888(3) | 11.1640(2), 14.2254(2), 37.2743(4) | 16.6294(3), 16.8479(3), 16.9793(3) |
| α, β, γ (°)      | 90.183(2) | 90, 90.183(3), 90 | 90, 90, 90 | 90, 90, 90 |
| V (Å³)           | 4778.4(2) | 6203.2(3) | 5919.62(15) | 4757.10(15) |
| Z                | 8     | 8    | 8    | 8     |
| f(000)           | 2048  | 3124 | 3280 | 2400  |
| Radiation type   | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| μ (mm⁻¹)         | 8.25  | 9.39 | 23.04 | 10.21 |
| Crystal colour and shape | Green rod | Yellow plate | Yellow plate | Red prism |
| Crystal size (mm) | 0.36 × 0.03 × 0.03 | 0.15 × 0.05 × 0.04 | 0.19 × 0.16 × 0.04 | 0.23 × 0.19 × 0.10 |
| Data collection  |       |      |      |       |
| Diffractometer   | Xcalibur, AtlasS2, Gemini ultra diffractometer | Xcalibur, Atlas, Gemini ultra diffractometer | Xcalibur, Atlas, Gemini ultra diffractometer | SuperNova, TitanS2 diffractometer |
| Absorption correction | Analytical | Analytical | Analytical | Gaussian |
| T_max, T_min     | 0.282, 0.824 | 0.382, 0.706 | 0.055, 0.424 | 0.189, 0.433 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 19437, 8317, 5864 | 49844, 5508, 4644 | 97078, 10506, 9981 | 10725, 4622, 3815 |
| Rint            | 0.042 | 0.040 | 0.042 | 0.034 |
| (sinθ/λ)max (Å⁻¹) | 0.596 | 0.597 | 0.597 | 0.624 |
| Range of h, k, l | h = -16→12, k = -13→14, l = -34→30 | h = -30→30, k = -22→22, l = -18→18 | h = -12→13, k = -16→16, l = -44→44 | h = -20→16, k = -8→20, l = -18→20 |
| Refinement       |       |      |      |       |
| R[F² > 2σ(F²)], wR(F²), S | 0.029, 0.055, 0.80 | 0.029, 0.075, 1.05 | 0.019, 0.047, 1.03 | 0.035, 0.088, 0.95 |
| No. of reflections | 8317 | 5508 | 10506 | 4622 |
| No. of parameters | 489  | 328  | 601  | 244  |
| No. of restraints | 0    | 1    | 0    | 0    |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.64, -0.31 | 0.97, -0.48 | 0.87, -0.62 | 0.74, -0.65 |

Computer programs: CrysAlis PRO, Agilent Technologies, SHELXL97 (Sheldrick, 1997), SHELXL2013 (Sheldrick, 2013), PLATON (Spek, 1990), PLATON (Spek, 2003).
|                  | 3-Cl’ | 3-Br | 5-Br | 5-I  |
|------------------|-------|------|------|------|
| CCDC Codes       | CCDC-1415114 | CCDC-1415116 | CCDC-1415117 | CCDC-1415118 |
| Chemical formula | C_{13}H_{13}ClCu_{2}FeP_{3} | C_{13}H_{13}Br_{2}Cu_{2}FeP_{3} | 0.15(C_{2}H_{4}) | C_{20}H_{20}Br_{2}Cu_{2}FeP_{3} | 0.5(C_{2}H_{4}) | C_{20}F_{20}Cu_{2}FeL_{2}P_{3} |
| M<sub>i</sub>    | 592.15 | 694.89 | 962.59 | 867.06 |
| Crystal system, space group | Monoclinic, P2<sub>1</sub>/c | Monoclinic, P2<sub>1</sub>/c | Triclinic, P1 | Monoclinic, P2<sub>1</sub>/n |
| Temperature (K)  | 123(2) | 123(2) | 123(2) | 123(1) |
| a, b, c (Å)      | 8.4412 (1), 16.8393 (2), 17.2062 (2) | 8.6057 (1), 16.8865 (1), 17.7057 (1) | 9.0546 (2), 10.6841 (2), 16.5146 (2) | 8.9909 (3), 31.8655 (12), 48.0476 (18) |
| α, β, γ (°)      | 90, 100.823 (1), 90 | 90, 99.799 (1), 90 | 76.978 (1), 78.518 (1), 85.863 (1) | 90, 93.688 (3), 90 |
| V (Å<sup>3</sup>) | 2402.25 (5) | 2535.46 (4) | 1600.55 (5) | 13737.1 (9) |
| Z                 | 4 | 4 | 2 | 20 |
| F(000)           | 1200 | 1374 | 946 | 8400 |
| Radiation type   | Cu Kα | Cu Kα | Cu Kα | Cu Kα |
| μ (mm<sup>-1</sup>) | 10.77 | 11.95 | 12.61 | 26.43 |
| Crystal colour and shape | Red cube | Purple prism | Green prism | Green-brown plate |
| Crystal size (mm) | 0.10 × 0.09 × 0.07 | 0.15 × 0.12 × 0.10 | 0.19 × 0.08 × 0.07 | 0.08 × 0.04 × 0.02 |
| Data collection  | Diffractometer | SuperNova, TitanS2 diffractometer | Xcalibur, AtlasS2, Gemini ultra diffractometer | Xcalibur, AtlasS2, Gemini ultra diffractometer | SuperNova, TitanS2 diffractometer |
| Absorption correction | Gaussian | Analytical | Analytical | Gaussian |
| T<sub>min</sub>, T<sub>max</sub> | 0.403, 0.562 | 0.254, 0.433 | 0.212, 0.533 | 0.302, 0.669 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 23102, 4828, 4271 | 37615, 4485, 4298 | 16570, 5643, 5219 | 84747, 27095, 11532 |
| R<sub>int</sub>   | 0.049 | 0.028 | 0.021 | 0.115 |
| (sin θ/λ) max (Å<sup>-1</sup>) | 0.624 | 0.596 | 0.596 | 0.624 |
| Range of h, k, l | h = -10→10, k = -20→20, l = -21→21 | h = -9→10, k = -20→20, l = -21→21 | h = -11→11, k = -12→12, l = -16→19 | h = -8→10, k = -34→39, l = -57→57 |
| Refinement       | R[F<sup>2</sup> > 2σ(F<sup>2</sup>), wR(F<sup>2</sup>), S] | 0.029, 0.074, 0.98 | 0.023, 0.054, 1.07 | 0.020, 0.049, 1.05 | 0.060, 0.148, 0.78 |
| No. of reflections | 4828 | 4485 | 5643 | 27095 |
| No. of parameters | 244 | 259 | 325 | 1401 |
| No. of restraints | 0 | 1 | 0 | 102 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δρ<sub>max</sub>, Δρ<sub>min</sub> (e Å<sup>-3</sup>) | 0.41, -0.73 | 0.58, -0.39 | 0.68, -0.45 | 1.92, -1.79 |

Computer programs: CrysAlis PRO, Agilent Technologies, SHELXL97 (Sheldrick, 1997), SHELXL2013 (Sheldrick, 2013), PLATON (Spek, 1990), PLATON (Spek, 2003).
Figure S1 Two symmetrically independent molecules in 2 (displacement parameters are at 50% level), hydrogen atoms are omitted for clarity. The iPr groups violating B lattice are encircled.

Table S4 Selected geometric parameters (Å) in 2.

|       |       |       |
|-------|-------|-------|
| Fe1—C13 | 2.065 (2) | Fe2—C36 | 2.100 (2) |
| Fe1—C16 | 2.082 (2) | Fe2—C27 | 2.114 (2) |
| Fe1—C17 | 2.084 (2) | Fe2—C23 | 2.135 (2) |
| Fe1—C14 | 2.093 (2) | Fe2—C31 | 2.146 (2) |
| Fe1—C15 | 2.099 (2) | Fe2—P4  | 2.2900 (6) |
| Fe1—C5  | 2.112 (2) | Fe2—P3  | 2.2988 (6) |
| Fe1—C1  | 2.137 (2) | P1—C9   | 1.766 (2)  |
| Fe1—C9  | 2.149 (2) | P1—C1   | 1.779 (2)  |
| Fe1—P1  | 2.2942 (6) | P2—C9  | 1.766 (2)  |
| Fe1—P2  | 2.2958 (6) | P2—C5  | 1.784 (2)  |
| Fe2—C38 | 2.076 (2) | P3—C31 | 1.761 (2)  |
| Fe2—C35 | 2.078 (2) | P3—C23 | 1.776 (2)  |
| Fe2—C39 | 2.081 (2) | P4—C31 | 1.764 (2)  |
| Fe2—C37 | 2.100 (2) | P4—C27 | 1.781 (2)  |
Figure S2 Two symmetrically independent molecules in 4 (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

Table S5 Selected geometric parameters (Å) in 4.

| Bond/Distance | Value   | Bond/Distance | Value   |
|---------------|---------|---------------|---------|
| Fe1—P1        | 2.3152 (6) | Fe2—P6       | 2.3157 (5) |
| Fe1—P2        | 2.3208 (5) | Fe2—C5⁺      | 2.1393 (19) |
| Fe1—P3        | 2.3201 (5) | P1—C5        | 1.788 (2) |
| Fe1—P4        | 2.3186 (6) | P1—C1        | 1.7745 (18) |
| Fe1—C1        | 2.1785 (19) | P2—C9       | 1.7832 (19) |
| Fe1—C5        | 2.1558 (18) | P2—C1        | 1.772 (2) |
| Fe1—C9        | 2.1456 (19) | P3—C13      | 1.773 (2) |
| Fe1—C13       | 2.1784 (19) | P3—C17      | 1.7834 (18) |
| Fe1—C17       | 2.1526 (18) | P4—C13      | 1.7713 (18) |
| Fe1—C21       | 2.1422 (18) | P4—C21     | 1.787 (2) |
| Fe2—C29⁺      | 2.1761 (19) | P5—C29⁺    | 1.773 (2) |
| Fe2—C33⁺      | 2.1489 (18) | P5—C25     | 1.7803 (19) |
| Fe2—C25       | 2.1393 (19) | P6—C29      | 1.7697 (18) |
| Fe2—C29       | 2.1761 (19) | P6—C33     | 1.789 (2) |
| Fe2—C33       | 2.1489 (18) | C5—C9     | 1.430 (3) |
| Fe2—P5⁺       | 2.3140 (5)  | C13—C14    | 1.523 (3) |
| Fe2—P6⁺       | 2.3157 (5)  | C17—C21   | 1.426 (3) |
| Fe2—P5         | 2.3140 (5) | C25—C33⁺  | 1.425 (3) |

Symmetry code(s): (i) -x, -y+2, -z+2.
**Figure S3** Two symmetrically independent molecules in the polymorph 5 (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

**Table S6** Selected geometric parameters (Å) in the polymorph 5.

|          | Fe1—P1  | Fe1—P2  | Fe1—P3  | Fe1—P4  | Fe1—P5  | Fe1—C1  | Fe1—C2  | Fe1—C3  | Fe1—C4  | Fe1—C5  | Fe1—C6  | Fe1—C7  | Fe1—C8  | Fe1—C9  | Fe1—C10 | Fe1—C11 | Fe1—C12 | Fe1—C13 | Fe1—C14 | Fe1—C15 | Fe1—C16 |
|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|          | 2.3594 (14) | 2.3604 (15) | 2.3210 (13) | 2.3222 (15) | 2.3215 (15) | 2.158 (5) | 2.193 (5) | 2.192 (5) | 2.152 (4) | 2.177 (5) | 2.174 (5) | 2.159 (5) | 2.3577 (15) | 2.3621 (14) | 2.3166 (13) |
|          | P1—P2  | P1—C1  | P2—C5  | P3—C1  | P3—C5  | P4—C9  | P5—C13 | P5—C17 | P6—P7  | P4—C17 | P5—C13 | P3—C5  | P4—C9  | P5—C13 | P3—C5  | P4—C17 | P5—C13 | P3—C5  | P4—C9  | P5—C13 | P3—C5  |
|          | 2.1343 (19) | 1.746 (5) | 1.770 (5) | 1.775 (5) | 1.750 (5) | 1.780 (5) | 1.766 (5) | 1.764 (5) | 2.1208 (19) | 1.765 (5) | 1.790 (6) | 1.777 (5) | 1.770 (5) | 1.781 (5) | 1.438 (7) | 1.440 (7) |
Figure S4 An independent molecule in the polymorph 5' (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

Table S7 Selected geometric parameters (Å) in 5'.

|       |       |       |       |
|-------|-------|-------|-------|
| Fe1—C4 | 2.1482 (14) | P1—C1 | 1.7631 (14) |
| Fe1—C2 | 2.1565 (14) | P1—C3 | 1.7801 (15) |
| Fe1—C1 | 2.1656 (14) | P2—C1 | 1.7695 (15) |
| Fe1—C3 | 2.1700 (14) | P2—C2 | 1.7857 (14) |
| Fe1—C5 | 2.1876 (14) | P3—C5 | 1.7585 (15) |
| Fe1—P1 | 2.3131 (4)  | P3—C4 | 1.7605 (14) |
| Fe1—P3 | 2.3177 (4)  | P4—C4 | 1.7675 (15) |
| Fe1—P2 | 2.3198 (4)  | P4—P5 | 2.1259 (5)  |
| Fe1—P5 | 2.3496 (4)  | P5—C5 | 1.7693 (15) |
| Fe1—P4 | 2.3678 (4)  | C2—C3 | 1.419 (2)   |
Figure S5 Two independent molecules in the polymorph 5'' (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

Table S8 Selected geometric parameters (Å) in the polymorph 5''.

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| Fe1—C11          | 2.164 (3) | Fe2—P25         | 2.319 (7) |
| Fe1—C12          | 2.165 (2) | P11—C11         | 1.761 (3) |
| Fe1—C14          | 2.175 (3) | P11—C12         | 1.762 (3) |
| Fe1—C13          | 2.157 (2) | P12—C12         | 1.772 (3) |
| Fe1—C15          | 2.156 (2) | P12—P13         | 2.1186 (9) |
| Fe1—P15          | 2.3188 (7) | P13—C11        | 1.769 (3) |
| Fe1—P14          | 2.3208 (7) | P14—C13        | 1.763 (3) |
| Fe1—P11          | 2.3271 (7) | P14—C14        | 1.794 (3) |
| Fe1—P12          | 2.3538 (7) | P15—C13        | 1.768 (3) |
| Fe1—P13          | 2.3612 (7) | P15—C15        | 1.785 (3) |
| Fe2—C21          | 2.159 (3) | P21—C21         | 1.761 (2) |
| Fe2—C22          | 2.158 (2) | P21—C22         | 1.762 (3) |
| Fe2—C23          | 2.157 (2) | P22—C21         | 1.772 (3) |
| Fe2—C24          | 2.154 (2) | P22—P23         | 2.1208 (9) |
| Fe2—C25          | 2.168 (2) | P23—C22         | 1.766 (3) |
| Fe2—P21          | 2.3212 (7) | P24—C23        | 1.768 (2) |
| Fe2—P22          | 2.3560 (7) | P24—C24        | 1.779 (3) |
| Fe2—P23          | 2.3613 (7) | P25—C23        | 1.756 (3) |
| Fe2—P24          | 2.3133 (7) | P25—C25        | 1.789 (2) |
Figure S6 An independent part in 2-Br (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

Table S9 Selected geometric parameters (Å) in 2-Br.

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| Cu1—N1        | 2.005 (3)    | Fe1—C2        | 2.090 (3)    |
| Cu1—P2        | 2.2123 (8)   | Fe1—C13       | 2.139 (3)    |
| Cu1—Br1       | 2.4955 (5)   | Fe1—C12       | 2.147 (3)    |
| Cu1—Br2       | 2.5394 (5)   | Fe1—C11       | 2.157 (3)    |
| N1—C21        | 1.129 (4)    | Fe1—P2        | 2.2681 (8)   |
| Cu2—P1        | 2.1735 (8)   | Fe1—P1        | 2.2719 (8)   |
| Cu2—Br1       | 2.3775 (5)   | P1—C11        | 1.751 (3)    |
| Cu2—Br2       | 2.3971 (5)   | P1—C13        | 1.772 (3)    |
| Fe1—C4        | 2.076 (3)    | P1—Cu2       | 2.1735 (8)   |
| Fe1—C1        | 2.078 (3)    | P2—C11        | 1.752 (3)    |
| Fe1—C5        | 2.080 (3)    | P2—C12        | 1.776 (3)    |
| Fe1—C3        | 2.083 (3)    |               |              |

Symmetry code(s): (i) -x+1/2, y+1/2, -z+1/2; (ii) -x+1/2, y-1/2, -z+1/2.
**Figure S7** An independent part in 2-I (displacement parameters are at 50% level), hydrogen atoms and MeCN solvent molecules are omitted for clarity.

**Table S10** Selected geometric parameters (Å) in 2-I.

| Bond           | Length (Å)  |
|----------------|-------------|
| Cu1—N1         | 2.010 (5)   |
| Cu1—P3         | 2.2380 (12) |
| Cu1—I2         | 2.6973 (8)  |
| Cu1—I1         | 2.7219 (9)  |
| N1—C1A         | 1.136 (7)   |
| Cu2—P2         | 2.2009 (12) |
| Cu2—I2         | 2.5288 (8)  |
| Cu2—I1         | 2.5371 (8)  |
| Cu3—P4         | 2.2165 (13) |
| Cu3—I3         | 2.5593 (7)  |
| Cu3—I4         | 2.5852 (8)  |
| Cu4—P1<sup>1</sup> | 2.1895 (13) |
| Cu4—I4         | 2.5332 (7)  |
| Cu4—I3         | 2.5463 (8)  |
| Fe1—C32        | 2.072 (5)   |
| Fe1—C33        | 2.082 (5)   |
| Fe1—C34        | 2.088 (5)   |
| Fe1—C31        | 2.093 (5)   |
| Fe1—C35        | 2.107 (6)   |
| Fe1—C11        | 2.156 (5)   |
| Fe1—C12        | 2.168 (5)   |
| Fe1—C13        | 2.193 (5)   |

Symmetry code(s): (i) -x+5/2, -y+1, z+1/2; (ii) -x+5/2, -y+1, z-1/2.
**Figure S8** An independent part in 3-Cl (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

**Figure S9** An independent part in 3-Cl' (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

**Table S11** Selected geometric parameters (Å) in 3-Cl and 3-Cl'.

|            | 3-Cl            | 3-Cl'           |
|------------|-----------------|-----------------|
| Cu1—Cu2    | 2.9509 (6)      | Cu1—Cu2        | 2.9957 (4) |
| Cu1—Cl1    | 2.3927 (8)      | Cu2—Cl1        | 2.3489 (6) |
| Cu1—Cl2    | 2.3541 (8)      | Cu1—Cl2        | 2.2416 (6) |
| Cu2—Cl1    | 2.2415 (8)      | Cu1—Cl1        | 2.2657 (6) |
| Cu2—Cl2    | 2.2658 (8)      | Cu2—Cl2        | 2.3977 (6) |
| Cu2—P1     | 2.1424 (8)      | Cu2—P1         | 2.2412 (6) |
| Cu1—P2ii   | 2.2587 (8)      | Cu2—P2ii       | 2.2587 (6) |
| Cu1—P3i    | 2.2332 (8)      | Cu1—P3i        | 2.1461 (6) |
| Fe1—C1     | 2.102 (3)       | Fe1—C1         | 2.075 (2)  |
| Fe1—C2     | 2.083 (3)       | Fe1—C2         | 2.073 (2)  |
| Fe1—C3     | 2.074 (3)       | Fe1—C3         | 2.109 (2)  |
| Bond                  | Distance (Å) |
|----------------------|--------------|
| Fe1—C4               | 2.108 (3)    |
| Fe1—C5               | 2.097 (3)    |
| Fe1—C11              | 2.155 (2)    |
| Fe1—C21              | 2.162 (2)    |
| Fe1—P1               | 2.3151 (6)   |
| Fe1—P2               | 2.3185 (6)   |
| P1—C11               | 1.758 (2)    |
| P1—C21               | 1.760 (2)    |
| P2—C3                | 1.742 (2)    |
| P2—P3                | 2.1091 (7)   |
| P2—Cuι               | 2.2587 (8)   |
| P3—C11               | 1.745 (2)    |
| P3—Cuιι              | 2.1461 (6)   |

Symmetry code(s) for 3-Cl: (i) -x+1/2, -y+1, z+1/2; (ii) x-1/2, y, -z+1/2; (iii) x+1/2, y, -z+1/2; (iv) -x+1/2, -y+1, z-1/2 and for 3-Cl': (i) -x, y-1/2, -z+1/2; (ii) -x, -y, -z; (iii) -x, y+1/2, -z+1/2.
Figure S10 An independent part in 3-Br (displacement parameters are at 50% level, hydrogen atoms and toluene solvent molecules are omitted for clarity).

Table S12 Selected geometric parameters (Å) in 3-Br.

| Bond          | Distance (Å) |
|---------------|--------------|
| Br1—Cu1       | 2.3716 (4)   |
| Br1—Cu2       | 2.5340 (4)   |
| Br2—Cu1       | 2.3844 (4)   |
| Br2—Cu2       | 2.4753 (4)   |
| Fe1—C2        | 2.074 (2)    |
| Fe1—C3        | 2.080 (2)    |
| Fe1—C5        | 2.107 (2)    |
| Fe1—C4        | 2.110 (2)    |
| Fe1—C1        | 2.110 (2)    |
| Fe1—C11       | 2.156 (2)    |
| Fe1—C21       | 2.169 (2)    |
| Fe1—P1        | 2.2886 (7)   |
| Fe1—P2        | 2.3164 (6)   |
| Cu1—P3        | 2.3232 (6)   |
| Cu2—P2        | 2.2600 (6)   |
| Cu2—P3        | 2.2769 (6)   |
| Cu1—P1        | 2.1686 (6)   |
| P2—C21        | 1.762 (2)    |
| P2—P3         | 2.1144 (8)   |
| P3—C11        | 1.765 (2)    |
| P3—Cu2        | 2.2770 (6)   |
| P1—C21        | 1.743 (2)    |
| P1—Cu1        | 1.746 (3)    |
| P1—Cu1        | 2.1685 (6)   |
| C3—C2         | 1.427 (3)    |

Symmetry code(s): (i) -x, -y+1, -z+1; (ii) -x, y-1/2, -z+3/2; (iii) -x, y+1/2, -z+3/2.
Figure S11 An independent part in 5-Br (displacement parameters are at 50% level, hydrogen atoms and toluene solvent molecules are omitted for clarity).

Table S13 Selected geometric parameters (Å) in 5-Br.

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| Cu1—P4                | 2.2186 (6)   |
| Cu1—Br1               | 2.3633 (4)   |
| Cu1—Br2               | 2.5124 (4)   |
| Cu1—Br2'              | 2.7118 (4)   |
| Cu2—P5                | 2.1885 (6)   |
| Cu2—Br1'              | 2.3800 (4)   |
| Cu2—Br3               | 2.4216 (4)   |
| Cu3—P2                | 2.2020 (6)   |
| Cu3—Br3               | 2.4933 (4)   |
| Cu3—Br3'              | 2.5169 (4)   |
| Cu3—Br2a              | 2.5267 (4)   |
| Br1—Cu2               | 2.3799 (4)   |
| Br2—Cu3               | 2.5267 (4)   |
| Br2—Cu1'              | 2.7118 (4)   |
| Br3—Cu3               | 2.5168 (4)   |
| Fe1—C3                | 2.164 (2)    |
| Fe1—C2                | 2.173 (2)    |
| Fe1—C1                | 2.175 (2)    |

Symmetry code(s): (i) -x, -y+1, -z+1; (ii) -x+1, -y+1, -z+1.
**Figure S12** An independent part in 5-I (displacement parameters are at 50% level, hydrogen atoms are omitted for clarity).

**Table S14** Selected geometric parameters (Å) in 5-I.

| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| Cu11—P11              | 2.265 (3)  | Fe22—C26              | 2.192 (13) |
| Cu11—I11              | 2.638 (2)  | Fe22—C30              | 2.194 (15) |
| Cu11—I11'             | 2.674 (2)  | Fe22—P27              | 2.304 (4)  |
| Cu11—Cu11'            | 2.834 (4)  | Fe22—P26              | 2.322 (4)  |
| Cu11—I12              | 2.963 (3)  | Fe22—P30              | 2.329 (4)  |
| Cu12—P13'             | 2.251 (3)  | Fe22—P29              | 2.336 (3)  |
| Cu12—I12              | 2.616 (2)  | Fe22—P28              | 2.343 (4)  |
| Cu12—I12''            | 2.666 (2)  | Fe31—C32              | 2.165 (13) |
| Cu12—I11              | 2.725 (2)  | Fe31—C34              | 2.171 (11) |
| Cu12—Cu12''           | 2.939 (4)  | Fe31—C33              | 2.176 (12) |
| Cu21—P21              | 2.264 (4)  | Fe31—C35              | 2.189 (12) |
| Cu21—I21              | 2.668 (2)  | Fe31—C31              | 2.208 (13) |
| Cu21—I24              | 2.680 (2)  | Fe31—P34              | 2.303 (4)  |
| Cu21—I22              | 2.923 (3)  | Fe31—P35              | 2.323 (4)  |
| Cu22—P23''            | 2.236 (4)  | Fe31—P33              | 2.332 (4)  |
| Cu22—I23              | 2.623 (2)  | Fe31—P31              | 2.345 (4)  |
| Cu22—I22              | 2.682 (2)  | Fe31—P32              | 2.351 (4)  |
| Bond Pair | Distance (Å) | Bond Pair | Distance (Å) | Bond Pair | Distance (Å) |
|-----------|--------------|-----------|--------------|-----------|--------------|
| Cu22—I24 viii | 2.709 (2) | Fe32—C38 | 2.142 (12) |
| Cu23—P29 | 2.250 (4) | Fe32—C37 | 2.152 (12) |
| Cu23—I22 | 2.614 (2) | Fe32—C39 | 2.163 (12) |
| Cu23—I23 | 2.689 (2) | Fe32—C36 | 2.170 (12) |
| Cu23—I21 | 2.711 (2) | Fe32—C40 | 2.224 (14) |
| Cu24—P27 | 2.273 (4) | Fe32—P36 | 2.309 (4) |
| Cu24—I24 | 2.673 (2) | Fe32—P37 | 2.320 (4) |
| Cu24—I21 | 2.698 (2) | Fe32—P39 | 2.337 (4) |
| Cu24—I23 viii | 2.875 (3) | Fe32—P38 | 2.338 (4) |
| Cu31—P31 | 2.251 (3) | Fe32—P40 | 2.348 (4) |
| Cu31—I31 | 2.633 (2) | P11—C11 | 1.758 (12) |
| Cu31—I34 viii | 2.665 (2) | P11—C13 | 1.767 (12) |
| Cu31—I32 | 2.731 (3) | P12—C11 | 1.765 (13) |
| Cu31—Cu34 viii | 3.006 (3) | P12—C12 | 1.782 (13) |
| Cu32—P36 | 2.266 (4) | P13—C15 | 1.747 (14) |
| Cu32—I32 | 2.668 (2) | P13—P14 | 2.122 (5) |
| Cu32—I33 | 2.714 (2) | P13—Cu12 ii | 2.251 (3) |
| Cu32—I31 | 2.850 (3) | P14—C14 | 1.787 (12) |
| Cu32—Cu33 | 2.919 (3) | P15—C14 | 1.755 (13) |
| Cu33—P34 | 2.260 (4) | P15—C15 | 1.769 (14) |
| Cu33—I33 | 2.616 (2) | P21—C21 | 1.751 (13) |
| Cu33—I32 | 2.644 (2) | P21—C23 | 1.772 (13) |
| Cu33—I34 | 3.105 (3) | P22—C21 | 1.794 (14) |
| Cu34—P39 | 2.250 (3) | P22—C22 | 1.802 (14) |
| Cu34—I34 | 2.598 (2) | P23—C25 | 1.781 (14) |
| Cu34—I31 viii | 2.683 (2) | P23—P24 | 2.127 (5) |
| Cu34—I33 | 2.718 (2) | P23—Cu22 viii | 2.236 (4) |
| Cu34—Cu31 viii | 3.006 (3) | P24—C24 | 1.764 (13) |
| I11—Cu11 i | 2.674 (2) | P25—C24 | 1.757 (15) |
| I12—Cu12 ii | 2.666 (2) | P25—C25 | 1.767 (14) |
| I23—Cu24 viii | 2.875 (3) | P26—C26 | 1.770 (14) |
| I24—Cu22 viii | 2.709 (2) | P26—C28 | 1.772 (12) |
| I31—Cu34 viii | 2.683 (2) | P27—C26 | 1.762 (13) |
| I34—Cu31 viii | 2.665 (2) | P27—C27 | 1.774 (14) |
| Fe11—C13 | 2.151 (11) | P28—C29 | 1.759 (13) |
| Fe11—C14 | 2.173 (11) | P28—P29 | 2.112 (5) |
| Fe11—C15 | 2.183 (13) | P29—C30 | 1.750 (14) |
| Fe11—C11 | 2.187 (13) | P30—C30 | 1.758 (14) |
| Fe11—C12 | 2.188 (11) | P30—C29 | 1.773 (15) |
| Fe11—P11 | 2.306 (3) | P31—C31 | 1.757 (15) |
| Fe11—P12 | 2.328 (3) | P31—P32 | 2.121 (5) |
| Fe11—P15  | 2.336 (4) | P32—C32 | 1.777 (14) |
|----------|----------|---------|------------|
| Fe11—P13 | 2.341 (3) | P33—C32 | 1.759 (14) |
| Fe11—P14 | 2.360 (4) | P33—C31 | 1.765 (14) |
| Fe21—C23 | 2.143 (11) | P34—C33 | 1.760 (12) |
| Fe21—C22 | 2.152 (12) | P34—C34 | 1.781 (13) |
| Fe21—C21 | 2.170 (14) | P35—C33 | 1.770 (13) |
| Fe21—C24 | 2.176 (12) | P35—C35 | 1.774 (14) |
| Fe21—C25 | 2.202 (14) | P36—C36 | 1.736 (13) |
| Fe21—P21 | 2.309 (4) | P36—C38 | 1.777 (14) |
| Fe21—P22 | 2.318 (4) | P37—C37 | 1.790 (14) |
| Fe21—P25 | 2.333 (4) | P37—C36 | 1.797 (13) |
| Fe21—P23 | 2.348 (4) | P38—C39 | 1.769 (15) |
| Fe21—P24 | 2.355 (4) | P38—C40 | 1.785 (14) |
| Fe22—C28 | 2.151 (11) | P39—C40 | 1.751 (14) |
| Fe22—C27 | 2.166 (12) | P39—P40 | 2.120 (5) |
| Fe22—C29 | 2.170 (14) | P40—C39 | 1.745 (14) |

Symmetry code(s): (i) -x+1, -y, -z+1; (ii) -x+2, -y, -z+1; (iii) x+1, y, z; (iv) x-1, y, z.

1. NMR Figure

![NMR Figure](image)

Figure S13 $^31$P/$^1$H NMR spectra of the respective fractions (F1 – F5) after the second column chromatographic work-up of a mixture of 2 and 3.

References

1. G. M. Sheldrick. Acta Cryst. (2015). C71, 3-8.
2. Olex2 v1.2-beta © OlexSys Ltd. 2004 – 2015