Supplementary information for the manuscript

Giant Rugby Ball [{CpBnFe(η⁵-P₅)}₂₄Cu₉₆Br₉₆] derived from Pentaphosphaferrocene and CuBr₂

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1. Experimental Part

All reactions were performed under an inert atmosphere of dry nitrogen or argon with standard vacuum, Schlenk, and glove-box techniques. Solvents were purified, dried and degassed prior to use by standard procedures. Compound I was synthesized following the reported procedure.¹ CuBr₂ was commercially available (Honeywell Riedel-de Haen) and was used without further purification. Solution NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ³¹P{¹H} MAS NMR spectrum was measured on a Bruker Avance 300. The corresponding ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer, while the elemental analysis was performed on a Vario EL III apparatus.

Synthesis of I:
In a Schlenk tube I (50 mg, 0.07 mmol) and CuBr₂ (31 mg, 0.14 mmol) are dissolved in CH₂Cl₂ (8 mL) and CH₃CN (6 mL). The immediately dark red solution is stirred for one day, before the solvent is completely removed. The red residue is dissolved in pure CH₂Cl₂ (15 mL), filtered and layered with toluene (10 mL). After diffusion a small amount of crystals of I can be obtained at the bottom of the Schlenk tube. The yield is increased by layering the solvent mixture with Et₂O resulting in the crystallization of red rods below the phase boundary. Mostly, also black blocks of the 80-vertex supramolecule II crystallize, sometimes even as a single phase.² It turned out that the amount of CH₃CN is determining: It is crucial for the formation of I, however only small amounts (at least less than the amount of CH₂Cl₂) are needed. Otherwise (without or too much CH₃CN) the formation of II is obtained exclusively. Although compounds I and II significantly differ in their copper content (molar ratio Cu:I = 4.0 in I; 1.7 in II) a stoichiometric control of the starting materials was without any influence. Gratifyingly, due to different color and shape of the crystals, I and II can be separated mechanically under the microscope. After diffusion the crystals are washed with hexane (5 x 5 mL) and dried in vacuum.

Analytical data of I:
Yield: varying on the amount of cocrystallized blocks of II, maximum: 38 mg (1.2 µmol, 84% referred to CuBr₂).
$^1$H NMR (CD$_2$Cl$_2$): $\delta$ [ppm] = 3.6 – 4.9 (m, br, 240 H, CH$_2$), 5.8 – 7.0 (m, br, 600 H, C$_6$H$_5$).

$^{31}$P{($^1$H)} NMR (CD$_2$Cl$_2$; NS = 10240): no signal detectable, see text.

$^{31}$P{($^1$H)} NMR (CD$_2$Cl$_2$; 193 K): no signal detectable, see text.

$^{31}$P{($^1$H)} MAS NMR: $\delta$ [ppm] = 155 (br, $\omega_{1/2}$ = 2460 Hz).

Positive ion ESI-MS (CH$_2$Cl$_2$): m/z = 1803.2 [{Cp$^{\text{Bn}}$Fe($\eta^5$-P$_5$)}$_2$Cu$_3$Br$_2$]$^+$, 1659.5 [{Cp$^{\text{Bn}}$Fe($\eta^5$-P$_5$)}$_2$Cu$_2$Br]$^+$, 1515.4 [{Cp$^{\text{Bn}}$Fe($\eta^5$-P$_5$)}$_2$Cu]$^+$.

Negative ion ESI-MS (CH$_2$Cl$_2$): m/z (%) = 510.4 (10) [Cu$_3$Br$_4$]$^-$, 366.4 (36) [Cu$_2$Br$_3$]$^-$, 222.5 (100) [CuBr$_2$]$^-$.

Elemental analysis: Calculated (%) for [C$_9$H$_8$Br$_9$Cl$_{12}$Cu$_9$Fe$_{24}$P$_{120}$] (31715 g/mol): C 36.58, H 2.71; found: C 35.62, H 2.97.

2. X-ray Structure Analysis

General Remarks:

Crystals of 1 were taken from a Schlenk flask under a stream of argon and immediately covered with 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. X-ray diffraction studies faced many challenges, since the crystals decompose rapidly losing solvent molecules and the collection of data at high theta angles required high exposure times. The data for 1 were collected on an Agilent Technologies SuperNova diffractometer equipped with Atlas$^{52}$ CCD detector and an SuperNova CuK$\alpha$ source ($\lambda$ = 1.54178 Å) using 0.5$^\circ$ $\omega$ scans at 123 K. Crystallographic data and details of the diffraction experiment are given in Table S1. The structure of 1 was solved by direct methods with SHEX97$^3$ and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using the multiprocessor and variable memory version SHEXL2013 with an increased to 5000 maximum number of full-matrix parameters. The structure was refined as an inversion twin with twin batches 0.515(5)/0.485(5). The non-hydrogen atoms were refined anisotropically if their occupancies exceeded 0.1 for heavy atoms (Cu, Br) or 0.8 for light atoms (C, N), while the hydrogen atoms were refined riding on pivot atoms. The enlarged displacement parameters for Cu and Br atoms indicated partial occupancies for several Cu$_x$Br$_y$ fragments. The disorder of the heavy part was refined as follows: The occupancies were refined with equated to average displacement parameters for the heavy atoms in the structure, U$_{iso}$=0.035. The occupancies were fixed at the resulting values and the refinement of the displacement parameters was performed. Many phenyl rings of the Cp$^{\text{Bn}}$ ligands are disordered via rotation around the CH$_2$-Ph bond over at least two positions and therefore were refined with restraint geometry. One entire Cp$^{\text{Bn}}$ ligand is disordered over two positions. Sometimes it was necessary to restrain also displacement parameters of the rotating Ph fragments as a result of unresolved disorder.
Some solvent molecules in 1 could be located from the difference Fourier map. The solvent molecules in most cases are disordered, and their molecular occupancy factors were refined using the FVAR instruction of SHELX with isotropic displacement parameters fixed at $U_{iso}=0.05$. The resulting occupancies were fixed and were refined isotropically due to the low molecular occupancy factors. Most of the toluene and dichloromethane molecules were refined with restraint geometry. The restraints were removed at the final stage of the refinement if possible. Due to the disorder the solvent content is generally underestimated. In the cavity only one MeCN and 0.8 CH$_2$Cl$_2$ molecules were localized. Using PLATON we estimated the possible amount of solvent molecules in the host cavity according to electron count of 1423. In addition to four localized positions of MeCN and four positions of CH$_2$Cl$_2$ in the cavity can include up to 20-21 MeCN or 11-12 CH$_2$Cl$_2$ molecules. There are cavities in the structure accessible for solvent molecules, however no residual electron density that can be attributed to some solvent molecule with reasonable geometry was found.

The packing motif for the supramolecules was calculated with TOPOSPro (Figure S1).  

A CIF file with comprehensive information on the details of the diffraction experiment and full tables of bond lengths and angles for 1 are deposited in Cambridge Crystallographic Data Centre under the deposition code CCDC-1408067.

**Table S I. Experimental details for compound 1**

|                             | 1                          |
|-----------------------------|----------------------------|
| CCDC Code                   | CCDC-1408067               |
| Chemical formula            | C$_{960}$H$_{840}$P$_{120}$Fe$_{24}$Cu$_{96}$Br$_{96}$·6.2(CH$_2$Cl$_2$)·4.6(C$_7$H$_8$)·2.4(CH$_3$CN) |
| $M_r$                       | 32345.16                   |
| Crystal system, space group | Orthorhombic, I222         |
| Temperature (K)             | 123(2)                     |
| $a$, $b$, $c$ (Å)           | 33.2127(2), 42.4597(2), 50.9189(3) |
| $V$ (Å$^3$)                 | 71805.9(7)                 |
| $Z$                         | 2                          |
| $F$(000)                    | 31517                      |
| Radiation type              | CuK$_\alpha$               |
| $\mu$ (mm$^{-1}$)           | 8.28                       |
| Crystal colour and shape    | Red-brown rod              |
| Crystal size (mm)           | 0.98 $\times$ 0.14 $\times$ 0.10 |
| Data collection             | SuperNova, Single source at offset, Atlas$^{52}$ |
| Absorption correction       | Gaussian                   |
| $T_{\text{min}}, T_{\text{max}}$ | 0.093, 0.535               |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 229206, 69900, 62895          |
|                  |       |
|------------------|-------|
| $R_{int}$        | 0.046 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.618 |
| Range of $h, k, l$ | $h = -37 \rightarrow 40, k = -52 \rightarrow 52, l = -62 \rightarrow 62$ |
| Refinement       |       |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.061, 0.175, 1.04 |
| No. of reflections | 69900 |
| No. of parameters | 3079  |
| No. of restraints | 46    |
| H-atom treatment | H-atom parameters constrained |
| $\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å$^{-3}$) | 3.31, -2.38 |
| Twin batch       | 0.515(5) |

Computer programs: CrysAlis PRO, Agilent Technologies, Version 1.171.37.31d (release 11-02-2014 CrysAlis171 .NET) (compiled Feb 11 2014, 18:09:27), SHELXS (Sheldrick, 1997), SHELXL2013 (Sheldrick, 2013).

Packing of the supramolecule 1
Disorder of the heavy atoms of the supramolecule 1

a) The disorder of the central part

The disorder of the central part is explained as a disorder between different orientations of the Cu₂ dimers with a probability of 0.75/0.25 (Fig. S1). There are four symmetrically related fragments involving Cu(1c)-Cu(2c) (0.75) and Cu(1d)-Cu(2d) that means that in three fragments position C and in one fragment position D realizes. In case of the dimer D the Cu(2d) atom coordinates three, not four, neighboring atoms. This, as well as the choice to be coordinated by two or three cyclo-P₅ ligands (1 and 2, or 1-3), can be a driving force for the disorder.

In addition very minor disorder is found for Cu(7), which appears with a 0.95/0.05 probability (Fig. S1b). The major position, denoted as Cu(7), are coordinated by the cyclo-P₅ ligand 3 in a η²-mode. The alternative minor positions Cu(7a) and Cu(7b) are coordinated by cyclo-P₅ ligands 3 and 4 in a η²- or η- mode, respectively. Cu(7b) also possesses triangular coordination environment.

b) The disorder of the capping groups

The disorder of the capping groups is much more complicated and related with the disorder by symmetry as well as positional disorder. The symmetry of the supramolecule is lower than its site symmetry (position 222 or D₂), and the caps on the different ends of the molecule are different and therefore overlap. The second
reason is an ability of Cu⁺ to have either a tetrahedral or trigonal environment, to form Cu₂ dimers, and to coordinate halogen atoms forming various architectures. Possible variants for the ordered cap are shown in Fig. S2. The disorder is very complicated even if the symmetry reasons are excluded and does not allow straightforward interpretation. The outlined variants can mix up and co-exist, if no contradictory distances appear.

Figure S2. a) The inorganic scaffold of the supramolecule (the disordered atoms are shown by lighter tint). The disordered caps are shown separately; b) The central fragment including disordered copper atoms.
Figure S3. Possible structure of the ordered cap in the supramolecule.
Table S2. Selected geometric parameters (Å) for 2

| Bond                  | Distance   | Bond                  | Distance   |
|-----------------------|------------|-----------------------|------------|
| Cu1—P17               | 2.273 (3)  | Cu3A—Br2A             | 2.433 (7)  |
| Cu1—P3                | 2.293 (3)  | Cu3A—Br3A             | 2.800 (7)  |
| Cu1—Br4              | 2.390 (2)  | Cu3A—Cu2B             | 2.97 (4)   |
| Cu1—Br5              | 2.459 (2)  | Cu2A—Br4              | 2.25 (2)   |
| Cu2—P2               | 2.218 (3)  | Cu2A—Br2A             | 2.37 (2)   |
| Cu2—Br6              | 2.345 (2)  | Cu2B—Br4              | 2.35 (3)   |
| Cu2—Br5              | 2.415 (3)  | Cu2B—Br3A             | 2.56 (4)   |
| Cu2—Br20             | 2.973 (3)  | Cu2B—Cu2B             | 2.81 (7)   |
| Cu3—P1               | 2.224 (3)  | Cu2B—Cu3A             | 2.97 (4)   |
| Cu3—Br8              | 2.414 (2)  | Br2A—Cu3A             | 2.433 (7)  |
| Cu3—Br7              | 2.420 (2)  | Br3A—Cu2A             | 2.43 (2)   |
| Cu3—Br9              | 2.725 (2)  | Br3A—Cu22             | 2.485 (2)  |
| Cu4—P27              | 2.219 (3)  | Br3A—Cu2B             | 2.56 (4)   |
| Cu4—Br26             | 2.393 (2)  | Br3A—Cu3A             | 2.800 (7)  |
| Cu4—Br25             | 2.521 (2)  | Cu3C—Br1C             | 2.46 (3)   |
| Cu4—Cu25             | 2.657 (3)  | Cu3C—Cu3D             | 2.55 (4)   |
| Cu4—Br7              | 2.736 (2)  | Cu3C—Br3C             | 2.57 (3)   |
| Cu4—Cu21             | 2.872 (2)  | Cu3C—Br1C             | 2.61 (3)   |
| Cu5—P6               | 2.335 (3)  | Cu3C—Br4              | 2.82 (3)   |
| Cu5—P7               | 2.376 (3)  | Cu3C—Cu22             | 2.84 (3)   |
| Cu5—Br10             | 2.4157 (19)| Cu3D—Br4              | 2.40 (3)   |
| Cu5—Br15             | 2.4416 (19)| Cu3D—Br1C             | 2.48 (3)   |
| Cu5—Br9              | 2.710 (2)  | Cu3D—Br1C             | 2.56 (3)   |
| Cu6—P7               | 2.260 (3)  | Cu3D—Cu4D             | 2.67 (4)   |
| Cu6—P15              | 2.293 (3)  | Cu3D—Cu3D             | 2.78 (7)   |
| Cu6—Br8              | 2.3512 (18)| Cu3D—Cu4D             | 2.93 (4)   |
| Cu6—Br9              | 2.725 (2)  | Br3C—Cu3C             | 2.57 (3)   |
| Cu7—P9               | 2.349 (3)  | Br3C—Cu22             | 2.689 (4)  |
| Cu7—P8               | 2.433 (3)  | Cu7A—P10              | 2.36 (3)   |
| Cu7—Br13             | 2.4997 (19)| Cu7A—P9               | 2.56 (3)   |
| Cu7—Br15             | 2.505 (2)  | Cu7A—Br15             | 2.78 (3)   |
| Cu7—Br14             | 2.566 (2)  | Cu7B—P11              | 2.20 (3)   |
| Cu9—P11              | 2.344 (3)  | Cu7B—Br15             | 2.28 (3)   |
| Cu9—P12              | 2.421 (3)  | Cu7B—Br14             | 2.31 (3)   |
| Cu9—Br18             | 2.4867 (19)| Cu7B—Br17             | 2.75 (3)   |
| Cu9—Br17             | 2.5069 (19)| Cu7B—Cu10             | 2.91 (3)   |
| Cu9—Br15             | 2.5115 (19)| Cu8—P10               | 2.221 (3)  |
| Cu3A—Br4             | 2.374 (6)  | Cu8—Br12              | 2.422 (2)  |
| Cu8—Br11             | 2.612 (2)  | Br4—Cu3C              | 2.82 (3)   |
| Bond                  | Distance (Å) 1   | Bond                  | Distance (Å) 2   | Bond                  | Distance (Å) 3   |
|----------------------|------------------|----------------------|------------------|----------------------|------------------|
| Cu8—Cu14             | 2.816 (2)        | Br11—Cu14           | 2.593 (2)        | Cu10—P24             | 2.236 (3)        |
| Cu10—P24             | 2.442 (2)        | Br24—Cu8           | 2.525 (2)        | Cu10—Br16            | 2.496 (2)        |
| Cu10—Br16            | 2.505 (2)        | Fe1—P4              | 2.356 (3)        | Cu10—Cu11            | 2.871 (3)        |
| Cu10—Cu11            | 2.248 (3)        | Fe1—P1              | 2.402 (3)        | Cu11—P12             | 2.253 (3)        |
| Cu11—P12             | 2.578 (2)        | Fe2—P7              | 2.319 (3)        | Cu11—Br16            | 2.770 (3)        |
| Cu11—Br16            | 2.622 (3)        | Fe2—P8              | 2.398 (3)        | Cu13—Br13            | 2.530 (2)        |
| Cu13—Br13            | 2.770 (3)        | Fe3—P11             | 2.361 (3)        | Cu13—Cu2C            | 2.770 (3)        |
| Cu13—Cu2C            | 2.262 (3)        | Fe3—P12             | 2.366 (3)        | Cu2C—Br27            | 2.458 (2)        |
| Cu2C—Br27            | 2.479 (2)        | Fe3—P15             | 2.371 (3)        | Cu2C—Br13            | 2.479 (2)        |
| Cu2C—Br13            | 2.622 (3)        | Fe4—P16             | 2.359 (3)        | Cu1D—Br27            | 2.424 (7)        |
| Cu1D—Br27            | 2.622 (7)        | Fe4—P18             | 2.364 (3)        | Cu1D—P30             | 2.499 (8)        |
| Cu1D—P30             | 2.513 (8)        | Fe4—P17             | 2.395 (3)        | Cu1D—Br13            | 2.513 (8)        |
| Cu1D—Br13            | 2.557 (9)        | Fe4—P20             | 2.404 (3)        | Cu1D—P23             | 2.557 (9)        |
| Cu1D—P23             | 2.874 (10)       | Fe5—P25             | 2.354 (3)        | Cu1D—Cu2D            | 2.874 (10)       |
| Cu1D—Cu2D            | 2.150 (6)        | Fe5—P22             | 2.367 (3)        | Cu2D—Br27            | 2.290 (6)        |
| Cu2D—Br27            | 2.319 (6)        | Fe5—P23             | 2.377 (3)        | Cu2D—Br24            | 2.856 (7)        |
| Cu2D—Br24            | 2.242 (7)        | Fe5—P21             | 2.412 (3)        | Cu14—P29             | 2.210 (3)        |
| Cu14—P29             | 2.248 (3)        | Fe6—P27             | 2.360 (3)        | Cu8—Br24             | 2.525 (2)        |
| Cu8—Br24             | 2.26 (2)         | Cu14—Br12           | 2.396 (2)        | Cu4D—Br5D            | 2.26 (2)         |
| Cu4D—Br5D            | 2.34 (2)         | Cu14—Br24           | 2.442 (2)        | Cu4D—Br5D            | 2.67 (4)         |
| Cu4D—Br5D            | 2.319 (6)        | Cu14—Br11           | 2.593 (2)        | Cu4D—Cu3D            | 2.719 (17)       |
| Cu4D—Cu3D            | 2.67 (4)         | Cu17—P26            | 2.233 (3)        | Br1C—Cu3C            | 2.46 (3)         |
| Cu4D—Br1C            | 2.48 (3)         | Cu17—Br22           | 2.558 (2)        | Br5D—Cu4D            | 2.26 (2)         |
| Br1C—Cu3C            | 2.39 (2)         | Cu18—Br23           | 2.406 (2)        | Br4—Cu2B             | 2.35 (4)         |
| Br5D—Cu4D            | 2.374 (6)        | Cu18—Br22           | 2.510 (2)        | Br4—Cu3A             | 2.390 (2)        |
| Br4—Cu2B             | 2.199 (3)        | Cu18—Br19           | 2.536 (2)        | Cu19—P16             | 2.249 (3)        |
| Bond                  | Distance (Å) | Error  | Bond                  | Distance (Å) | Error  |
|-----------------------|--------------|--------|-----------------------|--------------|--------|
| Cu19—Br20             | 2.3965       | 0.019  | P2—P3                 | 2.093        | 0.004  |
| Cu19—Br21             | 2.487        | 0.02   | P3—P4                 | 2.100        | 0.004  |
| Cu19—Br19             | 2.534        | 0.02   | P4—P5                 | 2.100        | 0.004  |
| Cu19—Cu20             | 2.946        | 0.013  | P6—P10                | 2.131        | 0.004  |
| Cu20—P14              | 2.218        | 0.013  | P6—P7                 | 2.204        | 0.004  |
| Cu20—Br6              | 2.369        | 0.02   | P7—P8                 | 2.129        | 0.004  |
| Cu20—Br20             | 2.380        | 0.02   | P8—P9                 | 2.156        | 0.004  |
| Cu21—P19i             | 2.255        | 0.02   | P9—P10                | 2.131        | 0.004  |
| Cu21—P5               | 2.267        | 0.02   | P10—Cu8ii             | 2.221        | 0.004  |
| Cu21—Br26             | 2.392        | 0.02   | P11—P15               | 2.134        | 0.004  |
| Cu21—Br25             | 2.5258       | 0.019  | P11—P12               | 2.174        | 0.004  |
| Cu22—P18i             | 2.246        | 0.02   | P12—P13               | 2.117        | 0.004  |
| Cu22—P4               | 2.251        | 0.02   | P13—P14               | 2.124        | 0.004  |
| Cu22—Br1C             | 2.272        | 0.05   | P14—P15               | 2.187        | 0.004  |
| Cu22—Br2A             | 2.441        | 0.02   | P16—P20               | 2.100        | 0.004  |
| Cu22—Br3A             | 2.485        | 0.02   | P16—P17               | 2.102        | 0.004  |
| Cu22—Br3C             | 2.689        | 0.04   | P17—P18               | 2.107        | 0.004  |
| Cu22—Cu2A             | 2.73         | 0.02   | P18—P19               | 2.095        | 0.004  |
| Cu22—Cu3Ci            | 2.84         | 0.03   | P18—Cu22i             | 2.246        | 0.004  |
| Cu24—P14              | 2.356        | 0.02   | P19—P20               | 2.098        | 0.004  |
| Cu24—P15              | 2.378        | 0.02   | P19—Cu21i             | 2.255        | 0.004  |
| Cu24—Br21             | 2.4510       | 0.018  | P21—P25               | 2.085        | 0.004  |
| Cu24—Br9              | 2.5070       | 0.018  | P21—P22               | 2.106        | 0.004  |
| Cu24—Br18             | 2.5520       | 0.019  | P21—Cu26ii            | 2.251        | 0.004  |
| Cu25—Br10             | 2.349        | 0.02   | P22—P23               | 2.117        | 0.004  |
| Cu25—Br7              | 2.434        | 0.02   | P22—Cu17iii           | 2.262        | 0.004  |
| Cu25—Br25             | 2.464        | 0.02   | P23—P24               | 2.074        | 0.005  |
| Cu26—P21iii           | 2.251        | 0.03   | P24—P25               | 2.074        | 0.004  |
| Cu26—Br18             | 2.432        | 0.02   | P25—Cu11iii           | 2.249        | 0.003  |
| Cu26—Br19             | 2.4377       | 0.018  | P26—P27               | 2.104        | 0.004  |
| Cu26—Br22             | 2.546        | 0.02   | P26—P30               | 2.115        | 0.004  |
| Fe6—P26               | 2.371        | 0.03   | P26—Cu17iii           | 2.233        | 0.004  |
| Fe6—P30               | 2.381        | 0.03   | P27—P28               | 2.097        | 0.004  |
| Fe6—P29               | 2.387        | 0.03   | P27—Cu4ii             | 2.219        | 0.003  |
| Fe6—P28               | 2.402        | 0.03   | P28—P29               | 2.066        | 0.004  |
| P1—P2                 | 2.095        | 0.004  | P29—P30               | 2.098        | 0.005  |
Figure S4: a) The distribution of the Cu-P-P bond angles for the different modes of the Cu coordination to the cyclo-P₅ ligand. The σ-coordination is mononodal (blue bars), while the π-coordination is binodal and represented by acute β and obtuse γ angles.

Figure S5: Stereogram of 1 to give a 3D impression of the scaffold (two offset images separately to the left and right eye).

3. NMR Spectroscopic investigations
Figure S6 $^{31}$P$_1^1$H NMR spectrum of crystals of 1 (NS = 1024) in CD$_2$Cl$_2$ at r.t.

Figure S7 $^{31}$P$_1^1$H NMR spectrum of crystals of 1 in CD$_2$Cl$_2$ at T = 193K.

Figure S8 $^{31}$P$_1^1$H MAS NMR spectrum of crystals of 1.
Figure S9: $^1$H NMR spectrum of 1 in CD$_2$Cl$_2$. * = CH$_2$Cl$_2$.

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