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Supplementary information for

Unexpected Fragmentation Reaction of Triphosphaferrocene: Formation of supramolecular assemblies containing the $(1,2,4\text{-}P_3C_2Mes_2)^-$ ligand

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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. [Cp*Fe(η^5-$P_3C_2Mes_2$)] was synthesized following the reported procedure. Commercially available chemicals were used without further purification. Solution NMR spectra were recorded on either Bruker Avance 300 or 400 spectrometer. The corresponding ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer, while elemental analyses were performed on a Vario EL III apparatus.

1.1 Synthesis of 2

In a thin Schlenk tube a solution of [Cp*Fe(η^5-$P_3C_2Mes_2$)] (30 mg, 0.06 mmol) in toluene (6 mL) is layered with a solution of CuCl (11 mg, 0.11 mmol) in CH_3CN (5 mL). After complete diffusion the solution is filtered and concentrated to 5 mL. Within a few weeks at room temperature red crystals of **2** · 6 CH_3CN can be obtained. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of **2**:

Yield: 12 mg (0.0058 mmol, 96%)

^{1}H NMR (CD_3CN): δ [ppm] = 2.06 (s, 6H, *o*-CH_3), 2.24 (s, 3H, *p*-CH_3), 6.88 (s, 2H, *aryl*-H).

^{13}C{^{1}H} NMR (CD_3CN): δ [ppm] = 20.97 (*o*-CH_3), 21.96 (*p*-CH_3), 127.96 (*aryl*-CH), 134.89 (*aryl*-$\underline{C}CH_3$), 135.92 (*aryl*-$\underline{C}CH_3$), 137.12 (*aryl*-C).

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 123.6 (br), 155.0 (br), 209.0 (br), 216.0 (br).

Positive ion ESI-MS (Et_2O/CH_3CN): *m/z* (%) = 2036.0 $[\{P_3C_2Mes_2\}_4Cu_8Cl_3]^+$, 1937.1 $[\{P_3C_2Mes_2\}_4Cu_7Cl_2]^+$, 1837.2 $[\{P_3C_2Mes_2\}_4Cu_6Cl]^+$, 1739.2 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1616.7 $[\{P_3C_2Mes_2\}_3Cu_7Cl_3]^+$, 1516.9 $[\{P_3C_2Mes_2\}_3Cu_6Cl_2]^+$, 1419.1 $[\{P_3C_2Mes_2\}_3Cu_5Cl]^+$, 1319.1 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1198.7 $[\{P_3C_2Mes_2\}_2Cu_6Cl_3]^+$, 1154.9 $[\{P_3C_2Mes_2\}_2Cu_4Cl\{Et_2O\}\{CH_3CN\}_2]^+$, 1055.0 $[\{P_3C_2Mes_2\}_2Cu_3\{Et_2O\}\{CH_3CN\}_2]^+$, 901.1 $[\{P_3C_2Mes_2\}Cu_5Cl_3\{CH_3CN\}_3]^+$, 801.2 $[\{P_3C_2Mes_2\}Cu_4Cl_2\{CH_3CN\}_3]^+$, 703.3 (100) $[\{P_3C_2Mes_2\}Cu_3Cl\{CH_3CN\}_3]^+$, 469.2 $[Cu_3Cl_2\{CH_3CN\}_3]^+$, 374.1 $[Cu_3Cl_2\{Et_2O\}\{CH_3CN\}]^+$, 333.0 $[Cu_3Cl_2\{Et_2O\}]^+$

Negative ion ESI-MS (Et_2O/CH_3CN): *m/z* (%) = 894.2 $[Cu_7Cl_8\{CH_2Cl_2\}\{CH_3CN\}_2]^-$, 866.2 $[Cu_8Cl_9\{CH_3CN\}]^-$, 796.1 $[Cu_6Cl_7\{CH_2Cl_2\}\{CH_3CN\}_2]^-$, 766.3 $[Cu_7Cl_8\{CH_3CN\}]^-$, 740.3 $[Cu_6Cl_7\{Et_2O\}\{CH_3CN\}]^-$, 668.2

$[Cu_6Cl_7\{CH_3CN\}]^-$, 640.4 $[Cu_5Cl_6\{Et_2O\}\{CH_3CN\}]^-$, 612.3 $[Cu_5Cl_6\{CH_3CN\}_2]^-$, 584.3 $[Cu_4Cl_5\{Et_2O\}\{CH_3CN\}_2]^-$, 542.5 $[Cu_3Cl_4\{CH_2Cl_2\}\{CH_3CN\}_3]^-$, 514.4 $[Cu_4Cl_5\{CH_3CN\}_2]^-$, 486.5 $[Cu_3Cl_4\{Et_2O\}\{CH_3CN\}_2]^-$, 414.5 $[Cu_3Cl_4\{CH_3CN\}_2]^-$, 386.4 $[Cu_2Cl_3\{Et_2O\}\{CH_3CN\}_2]^-$, 360.4 $[Cu_4Cl_3]^-$, 288.5 $[CuCl_2\{Et_2O\}\{CH_3CN\}_2]^-$, 232.6 $[Cu_2Cl_3]^-$, 134.6 (100) $[CuCl_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)_4Cl_{16}Cu_{20}(CH_3CN)_{11}]$ (3712.9 g/mol): C 32.99, H 3.28, N 4.15; found: C 32.02, H 3.37, N 4.55.

Analytical data of the mother liquor of **2** (after 2 hours of stirring):

Positive ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 2099.2 $[\{Cp^*Fe(P_3C_2Mes_2)\}_3Cu_5Cl_4]^+$, 1999.4 $[\{Cp^*Fe(P_3C_2Mes_2)\}_3Cu_4Cl_3]^+$, 1899.3 $[\{Cp^*Fe(P_3C_2Mes_2)\}_3Cu_3Cl_2]^+$, 1801.5 $[\{Cp^*Fe(P_3C_2Mes_2)\}_3Cu_2Cl]^+$, 1353.2 $[\{Cp^*Fe(P_3C_2Mes_2)\}_2Cu_3Cl_2]^+$, 1255.4 $[\{Cp^*Fe(P_3C_2Mes_2)\}_2Cu_2Cl]^+$, 1155.4 $[\{Cp^*Fe(P_3C_2Mes_2)\}_2Cu]^+$, 650.1 (100) $[\{Cp^*Fe(P_3C_2Mes_2)\}Cu\{CH_3CN\}]^+$, 546.1 $[Cp^*Fe(P_3C_2Mes_2)]^+$

Negative ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 332.5 $[Cu_3Cl_4]^-$, 232.6 (100) $[Cu_3Cl_4]^-$, 160.7 $[FeCl_3]^-$, 134.7 $[CuCl_2]^-$

EI-MS (70 eV): 326.2 (100) $[Cp^*_2Fe]$

1.2 Synthesis of 3

In a thin Schlenk tube a solution of $[Cp^*Fe(\eta^5\text{-}P_3C_2Mes_2)]$ (25 mg, 0.05 mmol) in CH_2Cl_2 (8 mL) is layered with a solution of CuBr (33 mg, 0.23 mmol) in CH_3CN (20 mL). After complete diffusion the solution is concentrated to 15 mL and layered with Et_2O. While storing at 8°C the formation of bright red plates of **3** · 6 CH_3CN can be observed. After complete diffusion the slightly turbid mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of **3**:

Yield: 28 mg (0.007 mmol, crystalline, 56% referred to $[Cp^*Fe(\eta^5\text{-}P_3C_2Mes_2)]$)

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.04 (s, 6H, *o*-CH_3), 2.14 (s, 6H, *o*-CH_3), 2.26 (s, 6H, *p*-CH_3), 6.90 (s, 4H, *aryl*-H).

^{13}C{^{1}H} NMR (CD_3CN): δ [ppm] = 21.11 (*p*-CH_3), 22.82 (*o*-CH_3), 128.60 (*aryl*-CH), 136.91 (*aryl*-$\underline{C}CH_3$), 138.31 (*aryl*-$\underline{C}CH_3$).

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 136.0 (br, (**3**)-2P), 160.2 (br, (**4**)-1P), 203.9 (br, (**4**)-2P), 217.3 (br, (**3**)-1P).

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 2455.0 $[\{P_3C_2Mes_2\}_4Cu_{10}Br_5]^+$, 2313.1 $[\{P_3C_2Mes_2\}_4Cu_9Br_4]^+$, 2169.2 $[\{P_3C_2Mes_2\}_4Cu_8Br_3]^+$, 2025.2 $[\{P_3C_2Mes_2\}_4Cu_7Br_2]^+$, 1881.4 $[\{P_3C_2Mes_2\}_4Cu_6Br_1]^+$, 1748.9 $[\{P_3C_2Mes_2\}_3Cu_7Br_3]^+$, 1648.1 $[\{P_3C_2Mes_2\}_3Cu_6Br_2\{CH_3CN\}]^+$, 1607.0 $[\{P_3C_2Mes_2\}_3Cu_6Br_2]^+$, 1506.2 $[\{P_3C_2Mes_2\}_3Cu_5Br\{CH_3CN\}]^+$, 1474.7 $[\{P_3C_2Mes_2\}_2Cu_7Br_4]^+$, 1463.3 $[\{P_3C_2Mes_2\}_3Cu_5Br]^+$, 1330.8 $[\{P_3C_2Mes_2\}_2Cu_6Br_3]^+$, 1319.3 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1230.0 $[\{P_3C_2Mes_2\}_2Cu_5Br_2\{CH_3CN\}]^+$, 1188.9 $[\{P_3C_2Mes_2\}_2Cu_5Br_2]^+$, 1127.2 $[\{P_3C_2Mes_2\}_2Cu_4Br\{CH_3CN\}_2]^+$, 1097.6 $[\{P_3C_2Mes_2\}Cu_6Br_4\{CH_3CN\}]^+$, 1054.5 $[\{P_3C_2Mes_2\}_2Cu_4Br]^+$, 953.7 $[\{P_3C_2Mes_2\}Cu_5Br_3\{CH_3CN\}]^+$, 144.9 (100) $[Cu\{CH_3CN\}_2]^+$

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 798.2 $[Cu_5Br_6]^-$, 654.4 $[Cu_4Br_5]^-$, 510.5 $[Cu_3Br_4]^-$, 366.4 $[Cu_2Br_3]^-$, 222.5 (100) $[CuBr_2]^-$

1.3 Synthesis of 4

In a thin Schlenk tube a solution of $[Cp^*Fe(\eta^5\text{-}P_3C_2Mes_2)]$ (50 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) is layered with a solution of CuBr (129 mg, 0.9 mmol) in CH_3CN (5 mL). During diffusion the formation of small orange-red plates of **4** · CH_3CN and a small amount of bright yellow plates of $[Cu(CH_3CN)Br]_n$ (identification by unit cell parameters and comparison with CCDC data base) due to the excess of CuBr can be observed.

After complete diffusion the slightly turbid mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) dried in vacuo. The small amount of big bright plates of $[Cu(CH_3CN)Br]_n$ can easily be removed mechanically under the microscope to give pure **4**.

Analytical data of **4**:

Yield: 85 mg (0.041 mmol, crystalline, 92% referred to [Cp*Fe(η^5-$P_3C_2Mes_2$)])

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.04 (s, 6H, *o*-CH_3), 2.14 (s, 6H, *o*-CH_3), 2.26 (s, 6H, *p*-CH_3), 6.90 (s, 4H, *aryl*-H).

^{13}C{^{1}H} NMR (CD_3CN): δ [ppm] = 21.11 (*p*-CH_3), 22.82 (*o*-CH_3), 128.60 (*aryl*-CH), 136.91 (*aryl*-CCH_3), 138.31 (*aryl*-CCH_3).

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 136.0 (br, (**3**)-2P), 160.2 (br, (**4**)-1P), 203.9 (br, (**4**)-2P), 217.3 (br, (**3**)-1P).

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 3438.2 $[\{P_3C_2Mes_2\}_4Cu_{17}Br_{12}]^+$, 3293.4 $[\{P_3C_2Mes_2\}_4Cu_{16}Br_{11}]^+$, 3163.0 $[\{P_3C_2Mes_2\}_4Cu_{15}Br_{10}]^+$, 3019.1 $[\{P_3C_2Mes_2\}_4Cu_{14}Br_9]^+$, 2873.1 $[\{P_3C_2Mes_2\}_4Cu_{13}Br_8]^+$, 2733.1 $[\{P_3C_2Mes_2\}_4Cu_{12}Br_7]^+$, 2591.2 $[\{P_3C_2Mes_2\}_4Cu_{11}Br_6]^+$, 2457.2 $[\{P_3C_2Mes_2\}_4Cu_{10}Br_5]^+$, 2313.0 $[\{P_3C_2Mes_2\}_4Cu_9Br_4]^+$, 2169.1 $[\{P_3C_2Mes_2\}_4Cu_8Br_3]^+$, 2025.1 $[\{P_3C_2Mes_2\}_4Cu_7Br_2]^+$, 1881.3 (100) $[\{P_3C_2Mes_2\}_4Cu_6Br_1]^+$, 1739.4 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1647.9 $[\{P_3C_2Mes_2\}_3Cu_6Br_2\{CH_3CN\}]^+$, 1607.1 $[\{P_3C_2Mes_2\}_3Cu_6Br_2]^+$, 1504.2 $[\{P_3C_2Mes_2\}_3Cu_5Br\{CH_3CN\}]^+$, 1463.0 $[\{P_3C_2Mes_2\}_3Cu_5Br]^+$, 1328.6 $[\{P_3C_2Mes_2\}_2Cu_6Br_3]^+$, 1319.2 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1230.0 $[\{P_3C_2Mes_2\}_2Cu_5Br_2\{CH_3CN\}]^+$, 1188.9 $[\{P_3C_2Mes_2\}_2Cu_5Br_2]^+$, 1126.8 $[\{P_3C_2Mes_2\}_2Cu_4Br\{CH_3CN\}]^+$.

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 510.3 $[Cu_3Br_4]^-$, 366.5 $[Cu_2Br_3]^-$, 294.5 $[FeBr_3]^-$, 222.7 (100) $[CuBr_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)_2Cu_{9.3}Br_{7.3}(CH_3CN)_3]$ (2053.9 g/mol): C 28.07, H 2.75, N 2.73; found: C 27.64, H 2.96, N 3.28.

Analytical data of the mother liquor of **4**:

Positive ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 326.1 (100) $[Cp^*_2Fe]^+$, 273.0 $[Cp^*Fe\{CH_3CN\}_2]^+$, 232.1 $[Cp^*Fe\{CH_3CN\}]^+$

Negative ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 798.2 $[Cu_5Br_6]^-$, 741.0 $[Fe_3Br_7O]^-$, 726.3 $[Fe_3Br_7]^-$, 654.4 $[Cu_4Br_5]^-$, 510.4 $[Cu_3Br_4]^-$, 375.4 $[FeBr_4]^-$, 366.4 $[Cu_2Br_3]^-$, 294.5 (100) $[FeBr_3]^-$, 222.5 $[CuBr_2]^-$

EI-MS (70 eV): 326.2 $[Cp^*_2Fe]$

After 5 minutes of stirring:

^{1}H NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 1.61 (s, 15H, Cp*), 2.21 (s, 6H, *p*-CH_3), 2.74 (s, 12H, *o*-CH_3), 6.91 (s, 4H, *aryl*-H).

After 4 hours of stirring:

^{1}H NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 1.60 (s, 15H, Cp*), 1.69 (s, Cp^*_2Fe), 2.21 (s, 6H, *p*-CH_3), 2.75 (s, 12H, *o*-CH_3), 6.92 (s, 4H, *aryl*-H).

1.4 Synthesis of 5

In a thin Schlenk tube a solution of [Cp*Fe(η^5-$P_3C_2Mes_2$)] (25 mg, 0.05 mmol) in CH_2Cl_2 (8 mL) is layered with a solution of CuBr (22 mg, 0.15 mmol) in CH_3CN (20 mL). After complete diffusion the solution is concentrated to 15 mL and layered with Et_2O. Already during the diffusion process the formation of red crystals of **5** · 2 CH_3CN can be observed. After complete diffusion the slightly turbid mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of **5**:

Yield: 30 mg (0.006 mmol, crystalline, 96% referred to [Cp*Fe(η^5-$P_3C_2Mes_2$)])

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.02 (s, 12H, *o*-CH_3), 2.25 (s, 6H, *p*-CH_3), 5.44 (s, CH_2Cl_2), 6.87 (s, 4H, *aryl*-H).

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 2171.2 $[\{P_3C_2Mes_2\}_4Cu_8Br_3]^+$, 2025.3 $[\{P_3C_2Mes_2\}_4Cu_7Br_2]^+$, 1881.4 $[\{P_3C_2Mes_2\}_4Cu_6Br]^+$, 1739.4 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1646.4 $[\{P_3C_2Mes_2\}_3Cu_6Br_2\{CH_3CN\}]^+$, 1319.1 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1014.1 $[\{P_3C_2Mes_2\}_4Cu_7Br\{CH_3CN\}_2]^{2+}$, 993.2 $[\{P_3C_2Mes_2\}_4Cu_7Br\{CH_3CN\}]^{2+}$, 985.3$[\{P_3C_2Mes_2\}_2Cu_{11}Br_2\{CH_3CN\}]^{2+}$, 973.0 $[\{P_3C_2Mes_2\}_4Cu_7Br]^{2+}$, 963.3 $[\{P_3C_2Mes_2\}_4Cu_6\{CH_3CN\}_3]^{2+}$, 942.2 $[\{P_3C_2Mes_2\}_4Cu_6\{CH_3CN\}_2]^{2+}$, 920.6 $[\{P_3C_2Mes_2\}_4Cu_6\{CH_3CN\}]^{2+}$, 901.2 $[\{P_3C_2Mes_2\}_4Cu_6]^{2+}$

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 304.6 (100) $[Cu_2Br_2O]^-$, 222.7 $[CuBr_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)_8Cu_{16}Br_8(CH_3CN)_7(CH_2Cl_2)_3]$ (5040.7 g/mol): C 42.18, H 4.06, N 1.95; found: C 41.99, H 4.03, N 2.02.

1.5 Synthesis of 6

A solution of [Cp*Fe(η^5-$P_3C_2Mes_2$)] (110 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) is added to a solution of CuI (50 mg, 0.26 mmol) in CH_3CN (25 mL). After stirring the reaction mixture for 2 h, it is filtered (The residual solid still contains [Cp*Fe(η^5-$P_3C_2Mes_2$)], since an excess was used) and layered with Et_2O. After complete diffusion at -28°C red plates of **6** · 0.5 C_7H_8 · 2.5 CH_3CN can be obtained. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo. By concentrating the mother liquor and storing at -28 °C a second crop of crystals can be obtained.

Analytical data of **6**:

Yield: 40 mg (0.031 mmol, crystalline, 59% referred to CuI)

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.04 (s, 3H, *p*-CH_3), 2.13 (s, 3H, *p*-CH_3), 2.22 (s, 6H, *o*-CH_3), 2.27 (s, 6H, *o*-CH_3), 6.90 (s, 4H, *aryl*-H).

^{13}C{^{1}H} NMR (CD_3CN): δ [ppm] = 21.14, 23.50, 26.23, 128.66, 136.86, 138.37.

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 134 (br), 153.0 (br), 205 (br), 224 (br).

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 2883.2 $[\{P_3C_2Mes_2\}_4Cu_{11}I_6]^+$, 2878.2 $[\{P_3C_2Mes_2\}_3Cu_{12}I_8]^+$, 2691.5 $[\{P_3C_2Mes_2\}_4Cu_{10}I_5]^+$, 2650.4 $[\{P_3C_2Mes_2\}_3Cu_{11}I_7]^+$, 2500.1 $[\{P_3C_2Mes_2\}_4Cu_9I_4]^+$, 2463.1 $[\{P_3C_2Mes_2\}_3Cu_{10}I_6]^+$, 2424.7 $[\{P_3C_2Mes_2\}_2Cu_{11}I_8]^+$, 2312.7 $[\{P_3C_2Mes_2\}_3Cu_{12}I_8]^+$, 2273.0 $[\{P_3C_2Mes_2\}_3Cu_9I_5]^+$, 2234.7 $[\{P_3C_2Mes_2\}_2Cu_{10}I_7]^+$, 2119.7 $[\{P_3C_2Mes_2\}_4Cu_7I_2]^+$, 2081.2 $[\{P_3C_2Mes_2\}_3Cu_8I_4]^+$, 2042.9 $[\{P_3C_2Mes_2\}_2Cu_9I_6]^+$, 1929.1 $[\{P_3C_2Mes_2\}_4Cu_6I]^+$, 1890.8 $[\{P_3C_2Mes_2\}_3Cu_7I_3]^+$, 1742.0 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1700.9 $[\{P_3C_2Mes_2\}_3Cu_6I_2]^+$, 1661.8 $[\{P_3C_2Mes_2\}_2Cu_7I_4]^+$, 1511.0 $[\{P_3C_2Mes_2\}_3Cu_5I]^+$, 1472.4 $[\{P_3C_2Mes_2\}_2Cu_6I_3]^+$, 1321.6 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1285.2 $[\{P_3C_2Mes_2\}_2Cu_5I_2]^+$, 1242.2 $[\{P_3C_2Mes_2\}Cu_6I_4]^+$, 1172.8 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}_2]^+$, 1131.8 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}]^+$, 1090.8 $[\{P_3C_2Mes_2\}_2Cu_4I]^+$, 1052.4 $[\{P_3C_2Mes_2\}Cu_5I_3]^+$

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 1270.1 $[Cu_6I_7]^-$, 1078.2 $[Cu_5I_6]^-$, 888.3 $[Cu_4I_5]^-$, 698.5 $[Cu_3I_4]^-$, 506.6 $[Cu_2I_3]^-$, 316.8 (100) $[CuI_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)Cu_5I_4(CH_3CN)_3]$ (1303.8 g/mol): C 23.96, H 2.40, N 3.22; found: C 23.96, H 2.50, N 3.28.

1.6 Synthesis of 7

In a schlenk tube a solution of [Cp*Fe(η^5-$P_3C_2Mes_2$)] (28 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) is layered with a solution of CuI (35 mg, 0.18 mmol) in CH_3CN (10 mL). After complete diffusion the solution is filtered, concentrated to 3 mL and layered onto a toluene solution (10 mL) in a thin schlenk tube. During diffusion the

formation of yellow crystals of **7** · 2 C_7H_8 can be observed. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of **7**:

Yield: 18 mg (0.01 mmol, crystalline, 41% referred to CuI)

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.26 (s, br, 18H, CH_3), 6.92 (s, 4H, *aryl*-H).

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 137.2 (br), 222.6 (br).

Negative ion ESI-MS (dme/CH_3CN): *m/z* (%) = 2108.7 $[\{P_3C_2Mes_2\}_2Cu_8I_7]^-$, 1957.0 $[\{P_3C_2Mes_2\}_2Cu_7I_6\{CH_3CN\}]^-$, 1916.7 $[\{P_3C_2Mes_2\}_2Cu_7I_6]^-$, 1726.9 $[\{P_3C_2Mes_2\}_2Cu_6I_5]^-$, 1536.8 $[\{P_3C_2Mes_2\}_2Cu_5I_4]^-$, 1498.6 $[\{P_3C_2Mes_2\}Cu_6I_6]^-$, 1344.9 $[\{P_3C_2Mes_2\}_2Cu_4I_3]^-$, 1306.6 $[\{P_3C_2Mes_2\}Cu_5I_5]^-$, 1116.7 $[\{P_3C_2Mes_2\}Cu_4I_4]^-$, 1268.2 $[Cu_6I_7]^-$, 1078.2 $[Cu_5I_6]^-$, 888.3 $[Cu_4I_5]^-$, 698.5 $[Cu_3I_4]^-$, 506.6 $[Cu_2I_3]^-$, 316.8 (100) $[CuI_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)Cu_7I_6(CH_3CN)_2$*1.5 $C_7H_8]$ (1782 g/mol): C 23.26, H 2.26, N 1.57; found: C 23.58, H 2.45, N 1.58.

1.7 Synthesis of 8 and 9

In a thin schlenk tube a solution of [Cp*Fe(η^5-$P_3C_2Mes_2$)] (25 mg, 0.046 mmol) in CH_2Cl_2 (8 mL) is layered with a solution of CuI (44 mg, 0.23 mmol) in CH_3CN (20 mL). After complete diffusion the solution is filtered, concentrated to 15 mL and layered with Et_2O (15 mL). During diffusion the formation of orange-red plates of **8** · 0.5 CH_2Cl_2 · 3 CH_3CN and uniquely red rods of **9** · 0.6 CH_2Cl_2 can be observed. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of **8** and **9**:

Yield: 28 mg (In the event, only **8** is present: 0.013 mmol, crystalline, 45% referred to CuI; in the event, only **9** is present: 0.011 mmol, crystalline, 35% referred to CuI; a calculation of the ratio of **8** and **9** cannot be made, since one compound is molecular (**8**), the other one polymeric (**9**).

^{1}H NMR (CD_3CN): δ [ppm] = 1.95 (s, CH_3CN), 2.04 (s, 3H, *p*-CH_3), 2.13 (s, 12H, *o*-CH_3), 2.20 (s, 6H, *o*-CH_3), 2.26 (s, 6H, *p*-CH_3), 6.90 (s, br, 6H, *aryl*-H).

^{31}P{^{1}H} NMR (CD_3CN): δ [ppm] = 135 (br), 206 (br), 223 (br).

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 2693.1 $[\{P_3C_2Mes_2\}_4Cu_{10}I_5]^+$, 2501.1 $[\{P_3C_2Mes_2\}_4Cu_9I_4]^+$, 2464.7 $[\{P_3C_2Mes_2\}_3Cu_{10}I_6]^+$, 2311.3 $[\{P_3C_2Mes_2\}_4Cu_8I_3]^+$, 2119.3 $[\{P_3C_2Mes_2\}_4Cu_7I_2]^+$, 2082.9 $[\{P_3C_2Mes_2\}_3Cu_8I_4]^+$, 1929.4 $[\{P_3C_2Mes_2\}_4Cu_6I]^+$, 1891.0 $[\{P_3C_2Mes_2\}_3Cu_7I_3]^+$, 1742.2 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1699.1 $[\{P_3C_2Mes_2\}_3Cu_6I_2]^+$, 1662.8 $[\{P_3C_2Mes_2\}_2Cu_7I_4]^+$, 1550.1 $[\{P_3C_2Mes_2\}_3Cu_5I\{CH_3CN\}]^+$, 1511.1 $[\{P_3C_2Mes_2\}_3Cu_5I]^+$, 1472.9 $[\{P_3C_2Mes_2\}_2Cu_6I_3]^+$, 1322.0 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1283.6 $[\{P_3C_2Mes_2\}_2Cu_5I_2]^+$, 1173.1 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}_2]^+$, 1132.0 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}]^+$, 1093.7 $[\{P_3C_2Mes_2\}_2Cu_4I]^+$, 996.1 $[\{P_3C_2Mes_2\}_4Cu_7I]^{2+}$, 901.1 $[\{P_3C_2Mes_2\}_4Cu_6]^{2+}$, 144.9 $[Cu\{CH_3CN\}_2]^+$

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 2944.9 $[\{P_3C_2Mes_2\}_4Cu_{10}I_7]^-$, 2908.5 $[\{P_3C_2Mes_2\}_3Cu_{11}I_9]^-$, 2867.8 $[\{P_3C_2Mes_2\}_2Cu_{12}I_{11}]^-$, 2759.2 $[\{P_3C_2Mes_2\}_4Cu_9I_6]^-$, 2720.5 $[\{P_3C_2Mes_2\}_3Cu_{10}I_8]^-$, 2678.4 $[\{P_3C_2Mes_2\}_2Cu_{11}I_{10}]^-$, 2563.1 $[\{P_3C_2Mes_2\}_4Cu_8I_5]^-$, 2524.7 $[\{P_3C_2Mes_2\}_3Cu_9I_7]^-$, 2488.3 $[\{P_3C_2Mes_2\}_2Cu_{10}I_9]^-$, 2374.3 $[\{P_3C_2Mes_2\}_4Cu_7I_4]^-$, 2335.1 $[\{P_3C_2Mes_2\}_3Cu_8I_6]^-$, 2298.4 $[\{P_3C_2Mes_2\}_2Cu_9I_8]^-$, 2260.1 $[\{P_3C_2Mes_2\}Cu_{10}I_{10}]^-$, 2145.0 $[\{P_3C_2Mes_2\}_3Cu_7I_5]^-$, 2108.6 $[\{P_3C_2Mes_2\}_2Cu_8I_7]^-$, 2068.1 $[\{P_3C_2Mes_2\}Cu_9I_9]^-$, 1954.9 $[\{P_3C_2Mes_2\}_3Cu_6I_4]^-$, 1916.8 $[\{P_3C_2Mes_2\}_2Cu_7I_6]^-$, 1878.3 $[\{P_3C_2Mes_2\}Cu_8I_8]^-$, 1767.1 $[\{P_3C_2Mes_2\}_3Cu_5I_3]^-$, 1726.7 $[\{P_3C_2Mes_2\}_2Cu_6I_5]^-$, 1688.3 $[\{P_3C_2Mes_2\}Cu_7I_7]^-$, 1650.0 $[Cu_8I_9]^-$, 1534.8 $[\{P_3C_2Mes_2\}_2Cu_5I_4]^-$, 1498.5 $[\{P_3C_2Mes_2\}Cu_6I_6]^-$, 1460.1 $[Cu_7I_8]^-$, 1346.9 $[\{P_3C_2Mes_2\}_2Cu_4I_3]^-$, 1306.6 $[\{P_3C_2Mes_2\}Cu_5I_5]^-$, 1270.2 $[Cu_6I_7]^-$, 1116.7 $[\{P_3C_2Mes_2\}Cu_4I_4]^-$, 1078.3 $[Cu_5I_6]^-$, 888.4 $[Cu_4I_5]^-$, 698.5 $[Cu_3I_4]^-$, 506.6 $[Cu_2I_3]^-$, 316.6 (100) $[CuI_2]^-$

Elemental analysis: Found: C 24.82, H 2.69, N 2.25. Neither an exact assignment nor a calculation of the ratio of **8** and **9** can be made, since one compound is molecular (**8**), the other one polymeric (**9**).

Analytical data of **8**:

Positive ion ESI-MS (CH_3CN): *m/z* (%) = 2693.1 $[\{P_3C_2Mes_2\}_4Cu_{10}I_5]^+$, 2501.1 $[\{P_3C_2Mes_2\}_4Cu_9I_4]^+$, 2462.7 $[\{P_3C_2Mes_2\}_3Cu_{10}I_6]^+$, 2311.2 $[\{P_3C_2Mes_2\}_4Cu_8I_3]^+$, 2274.7 $[\{P_3C_2Mes_2\}_3Cu_9I_5]^+$, 2119.2 $[\{P_3C_2Mes_2\}_4Cu_7I_2]^+$, 2082.8 $[\{P_3C_2Mes_2\}_3Cu_8I_4]^+$, 1929.4 $[\{P_3C_2Mes_2\}_4Cu_6I]^+$, 1891.0 $[\{P_3C_2Mes_2\}_3Cu_7I_3]^+$, 1740.1 $[\{P_3C_2Mes_2\}_4Cu_5]^+$, 1701.0 $[\{P_3C_2Mes_2\}_3Cu_6I_2]^+$, 1662.6 $[\{P_3C_2Mes_2\}_2Cu_7I_4]^+$, 1550.0 $[\{P_3C_2Mes_2\}_3Cu_5I\{CH_3CN\}]^+$, 1511.1 $[\{P_3C_2Mes_2\}_3Cu_5I]^+$, 1472.8 $[\{P_3C_2Mes_2\}_2Cu_6I_3]^+$, 1322.0 $[\{P_3C_2Mes_2\}_3Cu_4]^+$, 1283.6 $[\{P_3C_2Mes_2\}_2Cu_5I_2]^+$, 1173.0 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}_2]^+$, 1131.9 $[\{P_3C_2Mes_2\}_2Cu_4I\{CH_3CN\}]^+$, 1093.0 $[\{P_3C_2Mes_2\}_2Cu_4I]^+$, 996.2 $[\{P_3C_2Mes_2\}_4Cu_7I]^{2+}$, 901.2 $[\{P_3C_2Mes_2\}_4Cu_6]^{2+}$

Negative ion ESI-MS (CH_3CN): *m/z* (%) = 2562.5 $[\{P_3C_2Mes_2\}_4Cu_8I_5]^-$, 2528.7 $[\{P_3C_2Mes_2\}_3Cu_9I_7]^-$, 2490.2 $[\{P_3C_2Mes_2\}_2Cu_{10}I_9]^-$, 2373.2 $[\{P_3C_2Mes_2\}_4Cu_7I_4]^-$, 2334.9 $[\{P_3C_2Mes_2\}_3Cu_8I_6]^-$, 2296.4 $[\{P_3C_2Mes_2\}_2Cu_9I_8]^-$, 2144.7 $[\{P_3C_2Mes_2\}_3Cu_7I_5]^-$, 2106.7 $[\{P_3C_2Mes_2\}_2Cu_8I_7]^-$, 2070.2 $[\{P_3C_2Mes_2\}Cu_9I_9]^-$, 1954.9 $[\{P_3C_2Mes_2\}_3Cu_6I_4]^-$, 1916.5 $[\{P_3C_2Mes_2\}_2Cu_7I_6]^-$, 1878.3 $[\{P_3C_2Mes_2\}Cu_8I_8]^-$, 1841.8 $[Cu_9I_{10}]^-$, 1765.0 $[\{P_3C_2Mes_2\}_3Cu_5I_3]^-$, 1726.7 $[\{P_3C_2Mes_2\}_2Cu_6I_5]^-$, 1688.3 $[\{P_3C_2Mes_2\}Cu_7I_7]^-$, 1651.8 $[Cu_8I_9]^-$, 1534.7 $[\{P_3C_2Mes_2\}_2Cu_5I_4]^-$, 1498.3 $[\{P_3C_2Mes_2\}Cu_6I_6]^-$, 1460.1 $[Cu_7I_8]^-$, 1306.5 $[\{P_3C_2Mes_2\}Cu_5I_5]^-$, 1270.1 $[Cu_6I_7]^-$, 1116.6 $[\{P_3C_2Mes_2\}Cu_4I_4]^-$, 1078.2 $[Cu_5I_6]^-$, 888.5 $[Cu_4I_5]^-$, 698.5 $[Cu_3I_4]^-$, 506.6 $[Cu_2I_3]^-$, 316.6 (100) $[CuI_2]^-$

Elemental analysis: Calculated (%) for $[(P_3C_2Mes_2)_2Cu_8I_6(CH_3CN)_4]$ (2145 g/mol): C 26.88, H 2.63, N 2.61; found: C 26.59, H 2.69, N 2.70.

Analytical data of the mother liquor of **8** and **9**:

Positive ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 526.7 (100) $[Cu_3I_2\{CH_3CN\}_2]^+$, 432.1 $[Cp^*FeCu\{CH_3CN\}]^+$, 389.2 $[Cp^*FeCu]^+$, 334.7 $[Cu_2I\{CH_3CN\}_2]^+$, 326.1 (90) $[Cp^*_2Fe]^+$

Negative ion ESI-MS (CH_2Cl_2/CH_3CN): *m/z* (%) = 2411.5 $[Cu_{12}I_{13}]^-$, 2219.4 $[Cu_{11}I_{12}]^-$, 2031.6 $[Cu_{10}I_{11}]^-$, 1841.6 $[Cu_9I_{10}]^-$, 1649.8 $[Cu_8I_9]^-$, 1459.9 $[Cu_7I_8]^-$, 1270.1 $[Cu_6I_7]^-$, 1078.2 $[Cu_5I_6]^-$, 888.3 $[Cu_4I_5]^-$, 698.5 $[Cu_3I_4]^-$, 506.6 $[Cu_2I_3]^-$, 380.6 $[I_3]^-$, 316.7 (100) $[CuI_2]^-$

2. Solution NMR spectroscopic details

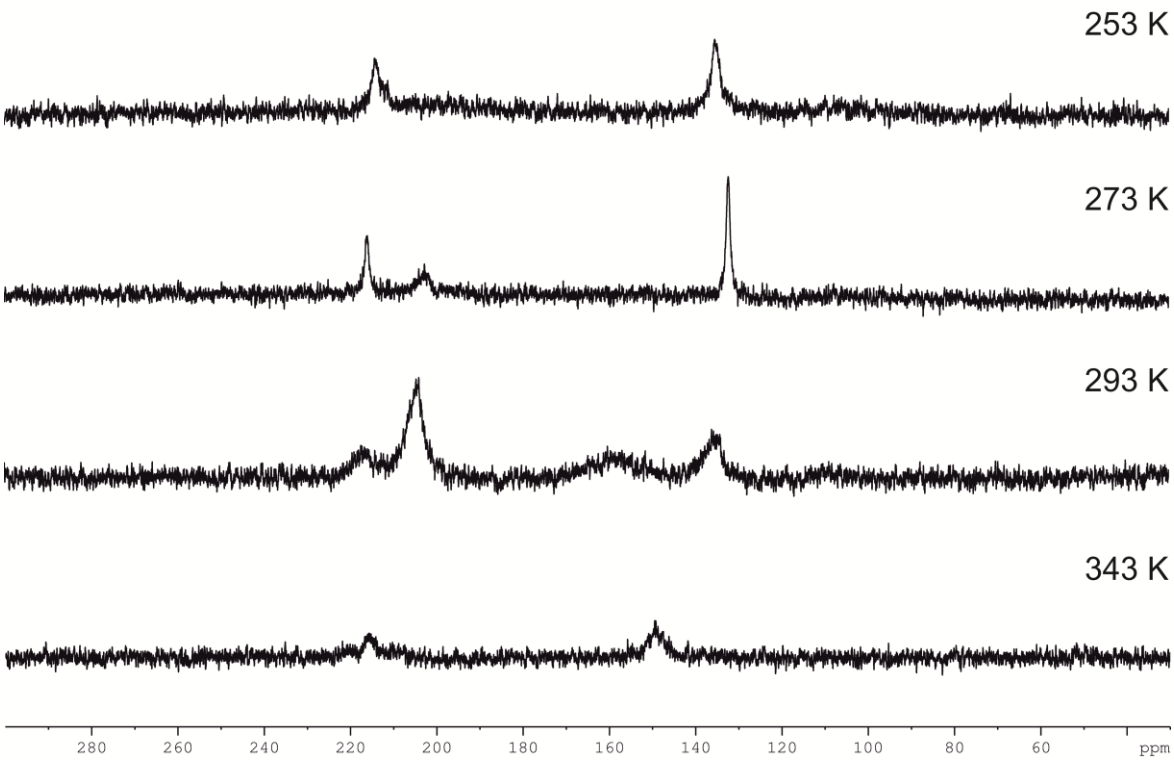


Fig. S 1: VT $^{31}P\{^{1}H\}$ NMR of freshly dissolved crystals of **3**.

3. X-ray structure analysis

The list of structurally investigated compounds:

$[\{Cu_7Cl_4(P_3C_2Mes_2)_2(MeCN)_7\}_2\{Cu_2Cl_2(MeCN)_2\}\{Cu_2Cl_3\}_2] \cdot 6\ CH_3CN$ (**2** · 6 CH_3CN)

$[\{Cu_7Br_4(P_3C_2Mes_2)_2(MeCN)_7\}_2\{Cu_2Br_2(MeCN)_2\}\{Cu_2Br_3\}_2] \cdot 6\ CH_3CN$ (**3** · 6 CH_3CN)

$[Cu_6Br_4(P_3C_2Mes_2)_2(MeCN)_{8.5}(CuBr)_{3.3(3)}] \cdot CH_3CN$ (**4** · CH_3CN)

$[\{Cu_5Br(MeCN)_5(P_3C_2Mes_2)_4Cu(MeCN)_2CuBr_2\}_2Cu(MeCN)_2][CuBr_2] \cdot 2\ CH_3CN$ (**5** · 2 CH_3CN)

$[Cu_4(MeCN)_4I_4)\{P_3C_2Mes_2\}(Cu(MeCN)_3)] \cdot 0.5\ C_7H_8 \cdot 2.5\ CH_3CN$ (**6** · 0.5 C_7H_8 · 2.5 CH_3CN)

$[Cu_4(MeCN)_4I_6)\{P_3C_2(Mes)_2\}(Cu(MeCN)_3)] \cdot 2\ C_7H_8$ (**7** · 2 C_7H_8)

$[(P_3C_2Mes_2)_2\{Cu(MeCN)_3\}_2\{CuI)\}_6] \cdot 0.5\ CH_2Cl_2 \cdot 3\ CH_3CN$ (**8** · 0.5 CH_2Cl_2 · 3 CH_3CN)

$[Cp^*Fe(MeCN)_3][(P_3C_2Mes_2)_2\{Cu(MeCN)_2\}\{CuI)\}_6] \cdot 0.6\ CH_2Cl_2$ (**9** · 0.6 CH_2Cl_2)

Crystals of **2-9** were taken from a Schlenk tube under a stream of argon and covered with mineral oil. The single crystal was taken to the pre-centered goniometer head with CryoMount® and directly attached to the diffractometer into a stream of cold nitrogen. The data for **2** · 6 CH_3CN, **6** · 0.5 C_7H_8 · 2.5 CH_3CN, **7** ·

2 C_7H_8 and **8** · 0.5 CH_2Cl_2 · 3 CH_3CN were collected on an Agilent Technologies Gemini R-Ultra diffractometer equipped with Ruby CCD detector and an Enhanced Ultra CuK_α sealed tube (λ = 1.54178 Å) using 1° ω scans. The data for **3** · 6 CH_3CN**, 4** · CH_3CN**, 5** · 2 CH_3CN were collected on an Agilent Technologies diffractometer equipped with Titan^{S2} CCD detector and a SuperNova CuK_α microfocus source using 1° ω scans. The data for **9** · 0.6 CH_2Cl_2 were collected on an Agilent Technologies diffractometer equipped with Atlas CCD detector and a SuperNova CuK_α microfocus source using 1° ω scans. All measurements were performed at 123 K. Crystallographic data and details of the diffraction experiments are given in Table S 1 - Table S 3. The structures of **2-9** were solved by direct methods with *SIR97*,[1] *SHELX97* or *SHELX2013*.[2] 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, whereas the hydrogen atoms were refined riding on pivot atoms.

The crystal structure of **4** · CH_3CN is severely disorderd (Fig.2S). The displacement parameters of the heavy atoms were set equal to U_{iso} = 0.05 A^{-2}, subsequently the occupancy factors were refined. Their resulting values were fixed and the refinement of the displacement parameters was performed. The model was checked to be non-contradictory. For this reason the occupancy factors of each disordered part of the structure were analysed to give no contradictions with occupancy factors of conflicting disordered components. The occupancy factors of all atoms in the environment of copper atoms were checked to be in agreement with the occupancy factors and coordination polyhedra of the copper atoms. The missing CH_3CN molecules were found from the difference electron density map. Several solvent CH_3CN molecules are also disordered.

The crystal of **5** · 2 CH_3CN appeared to be a racemic twin (ratio 0.64(2) /0.34(2)) in the space group *Pc*. The structure possesses disorder of the heavy part. To refine the occupancies of these heavy atoms, their isotropic displacement parameters were fixed at 0.05 A^{-2}. The refined values were fixed and the displacement parameters were also refined. The linear counter anion $[CuBr_2]^-$ is disordered over at least two positions with high displacement parameters. On one hand, no residual density was found to correspond to any position of another anion (for example, disordered Br^-) that would allow to reduce the occupancy factors for the $[CuBr_2]^-$ anion. On the other hand, further split of the Cu and Br positions did not give a satisfactory geometry of the anion. Therefore the disorder of the anion over two positions of the same relative weight was accepted as the only possibility to reach charge balance.

In **6** · 0.5 C_7H_8 · 2.5 CH_3CN one of the mesityl ligands and one of the coordinated MeCN group are disordered over two positions with a ratio of 0.5/0.5 and 0.45/0.55, respectively. Solvated MeCN and toluene molecules in **6** · 0.5 C_7H_8 · 2.5 CH_3CN are disordered each over two close positions with the same ratio of 0.5/0.5. In **8** · 0.5 CH_2Cl_2 · 3 CH_3CN and **9** · 0.6 CH_2Cl_2 solvated CH_2Cl_2 molecules partly (0.5 and 0.6) occupy their positions.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of

bond lengths and angles for **2-9** are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC 1043724 - CCDC 1043731, respectively.

Table S 1. Experimental details for compounds **2-4**

	2 · 6 CH_3CN	**3** · 6 CH_3CN	**4** · CH_3CN
CCDC Codes	CCDC 1043724	CCDC 1043726	CCDC 1043725
Chemical formula	$C_{112}H_{136}Cl_{16}Cu_{20}N_{16}P_{12}\cdot 6(C_2H_3N)$	$C_{112}H_{136}Br_{16}Cu_{20}N_{16}P_{12}\cdot 6(C_2H_3N)$	$C_{59}H_{72.50}Br_{7.33}Cu_{9.33}N_{9.50}P_6$
M_r	2081.17	4873.69	2279.51
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
Temperature (K)	173	123	123
a, b, c (Å)	14.7230(11), 16.4433(8), 17.7704(9)	14.7655 (4),16.7179(5), 17.9266(5)	30.3248 (7), 16.9395 (4), 16.0657 (3)
α, β, γ (°)	89.990(4), 83.485(5), 71.708(5)	90.321(2), 96.606(2), 108.593(2)	102.218 (2)
V (Å^3)	4055.5(4)	4162.1(2)	8065.8 (3)
Z	1	1	4
F(000)	2084	2372	4441
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	6.68	8.65	8.32
Crystal colour and shape	Orange-to-red plate	Orange block	Orange plate
Crystal size (mm)	0.15 × 0.10 × 0.04	0.13 × 0.07 × 0.04	0.14 × 0.12 × 0.06
Data collection			
Diffractometer	Oxford Diffraction Gemini Ultra diffractometer	SuperNova, TitanS2 diffractometer	Supernova, TitanS2 diffractometer
Absorption correction	Multi-scan	Gaussian	Gaussian
T_{min}, T_{max}	0.569, 1.000	0.627, 0.826	0.361, 0.658
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24323, 12422, 9915	25708, 15945, 11431	23524, 8030, 6220
R_{int}	0.030	0.051	0.063
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.574	0.625	0.624
Range of h, k, l	h = -16→16, k = -18→14, l = -20→20	h = -18→17, k = -20→15, l = -20→22	h = -37→35, k = -21→19, l = -18→19
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.127, 1.05	0.048, 0.125, 0.92	0.062, 0.175, 0.97
No. of reflections	12422	15945	8030
No. of parameters	897	897	517
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.20, -0.65	2.47, -1.56	2.15, -0.78

Computer programs: *CrysAlis PRO*, Agilent Technologies, *SIR97* (Altomare, 1999), *SHELXL97* (Sheldrick, 1997), *PLATON* (Spek, 1990), *PLATON* (Spek, 2003).

Table S 2. Experimental details for compounds **5-7**

	5 · 2 CH_3CN	**6** · 0.5 C_7H_8 · 2.5 CH_3CN	**7** · 2 C_7H_8
CCDC Codes	CCDC 1043727	CCDC 1043728	CCDC 1043729
Chemical formula	$C_{196}H_{230}Br_8Cu_{16}N_{18}P_{24}$	$C_{34}H_{43}Cu_5I_4N_7P_3 \cdot 0.5(C_7H_8) \cdot 2.5(C_2H_3N)$	$C_{49}H_{57}Cu_7I_6N_4P_3$
M_r	5237.17	1616.67	2001.07
Crystal system, space group	Monoclinic, *Pc*	Triclinic, $P\bar{1}$	Monoclinic, *C*2/*c*
Temperature (K)	123	123	123
a, *b*, *c* (Å)	26.6111 (4), 20.1860 (2), 23.5404 (3)	13.4384(3), 14.3484(2), 15.5780(4)	31.3947(18), 12.7194(5), 16.5419(8)
α, β, γ (°)	102.911 (2)	83.695(2), 77.946(2), 80.480(2)	109.401(6)
V (Å^3)	12325.5 (3)	2888.22 (11)	6230.5(6)
Z	2	2	4
F(000)	5272	1556	3780
Radiation type	Cu *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	4.80	19.88	26.92
Crystal shape	Orange prism	Red elongated plate	Yellow needle
Crystal size (mm)	0.25 × 0.13 × 0.04	0.20 × 0.11 × 0.04	0.24 × 0.04 × 0.04
Data collection			
Diffractometer	Supernova, TitanS2 diffractometer	Xcalibur, Ruby, Gemini ultra diffractometer	Xcalibur, Ruby, Gemini ultra diffractometer
Absorption correction	Gaussian	Gaussian	Analytical
T_{min}, T_{max}	0.415, 0.833	0.080, 0.521	0.178, 0.550
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	80558, 38117, 33313	31867, 10141, 9195	15147, 5489, 4289
R_{int}	0.032	0.027	0.043
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.621	0.596	0.597
Range of *h*, *k*, *l*	*h* = -25→32, *k* = -24→24, *l* = -26→29	*h* = -15→15, *k* = -16→12, *l* = -18→18	*h* = -37→33, *k* = -13→15, *l* = -12→19
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.059, 0.158, 1.02	0.026, 0.069, 1.05	0.044, 0.114, 1.01
No. of reflections	38117	10141	5489
No. of parameters	2350	688	324
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.23, -0.67	0.98, -2.12	2.84, -1.34

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.31d (release 11-02-2014 CrysAlis171 .NET) (compiled Feb 11 2014,18:09:27), SHEXLS-97, *SHELXL2014* (Sheldrick, 2014).

Table S 3. Experimental details for compounds **8-9**

	8 · 0.5 CH_2Cl_2 · 3 CH_3CN	**9** · 0.6 CH_2Cl_2
CCDC Codes	CCDC 1043730	CCDC 1043731
Chemical formula	$C_{58.50}H_{72}ClCu_8I_6N_9P_6$	$C_{60.6}H_{75.2}Cl_{1.2}Cu_7FeI_6N_5P_6$
M_r	2392.24	2364.12
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, $P2_1/n$
Temperature (K)	123	123
a, *b*, *c* (Å)	48.744(3), 12.3812(5), 30.1538(19)	12.5667(6), 29.4452(14), 21.7343(11)
β (°)	117.951 (9)	90.144 (5)
V (Å^3)	16075 (2)	8042.3 (7)
Z	8	4
F(000)	9144	4525
Radiation type	Cu *K*α	Cu *K*α
μ (mm^{-1})	22.11	23.26
Crystal shape	Plate	Rod
Colour	Red	Red
Crystal size (mm)	0.27 × 0.18 × 0.03	0.29 × 0.13 × 0.03
Data collection		
Diffractometer	Xcalibur, Ruby, Gemini ultra diffractometer	SuperNova, Single source at offset, Atlas diffractometer
Absorption correction	Analytical	Analytical
T_{min}, T_{max}	0.055, 0.556	0.069, 0.540
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	60525, 14144, 6817	27532, 15888, 12704
R_{int}	0.170	0.049
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.596	0.628
Range of *h*, *k*, *l*	*h* = -56→57, *k* = -14→14, *l* = -35→19	*h* = -10→15, *k* = -35→35, *l* = -26→27
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.067, 0.171, 0.79	0.047, 0.163, 1.05
No. of reflections	14144	15888
No. of parameters	815	815
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	3.19, -1.48	2.05, -1.89

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.35.21 (release 20-01-2012 CrysAlis171 .NET) (compiled Jan 23 2012,18:06:46), *SIR97* (Altomare, 1999), *SHELXL97* (Sheldrick, 1997), SXGRAPH (Farrugia, 1999), *PLATON* (Spek, 2003).

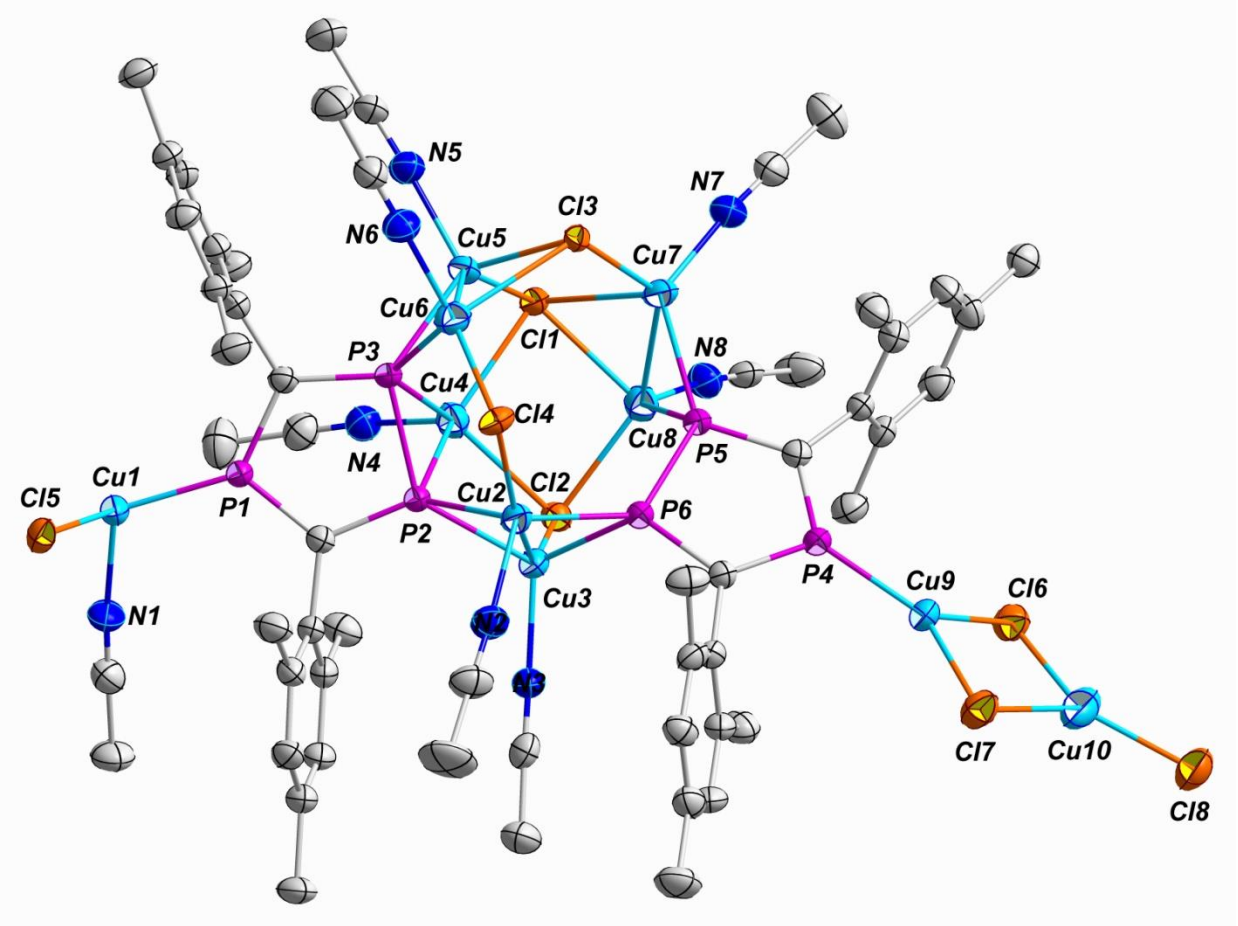


Fig. S 2. Independent part and numbering scheme in **2** · 6 CH_3CN. The hydrogen atoms are not shown.

Table S 4. Selected geometric parameters (Å, º) for **2** · 6 CH_3CN

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
Cu1—Cl5	2.3859 (13)	Cu8—Cl2	2.3942 (13)	Cu4—P3	2.5008 (14)	P4—C31	1.737 (4)
Cu1—P1	2.1733 (14)	Cu8—P5	2.2714 (15)	Cu4—N4	2.001 (5)	P5—P6	2.0984 (15)
Cu1—N1	2.004 (5)	Cu8—N8	1.963 (5)	Cu5—Cl1	2.4126 (14)	P5—C21	1.731 (5)
Cu1—Cl5^{i}	2.3682 (13)	Cu9—Cl6	2.2955 (15)	Cu5—Cl3	2.4376 (13)	P6—C31	1.727 (5)
Cu2—Cl4	2.3424 (13)	Cu9—Cl7	2.2496 (15)	Cu5—P3	2.2364 (13)	N1—C41	1.115 (8)
Cu2—P2	2.4059 (13)	Cu9—P4	2.1531 (15)	Cu5—N5	1.971 (4)	N2—C43	1.127 (7)
Cu2—P6	2.2915 (13)	Cu10—Cl6	2.2409 (17)	Cu6—Cl3	2.6260 (12)	N3—C45	1.134 (6)
Cu2—N2	1.987 (4)	Cu10—Cl7	2.4710 (17)	Cu6—Cl4	2.3172 (13)	N4—C47	1.138 (7)
Cu3—Cl2	2.3757 (13)	Cu10—Cl8	2.1363 (17)	Cu6—P3	2.3027 (13)	N5—C49	1.134 (7)
Cu3—P2	2.3158 (13)	P1—C1	1.725 (5)	Cu6—N6	1.958 (5)	N6—C51	1.125 (8)
Cu3—P6	2.3767 (13)	P1—C11	1.725 (4)	Cu7—Cl1	2.8403 (14)	N7—C53	1.130 (7)
Cu3—N3	1.979 (4)	P2—P3	2.1067 (15)	Cu7—Cl3	2.3033 (14)	N8—C55	1.122 (8)
Cu4—Cl1	2.4461 (13)	P2—C1	1.741 (4)	Cu7—P5	2.2213 (14)	N9—C57	1.140 (11)
Cu4—Cl2	2.5349 (14)	P3—C11	1.746 (5)	Cu7—N7	1.963 (4)	N10—C59	1.142 (9)
Cu4—P2	2.4187 (13)	P4—C21	1.735 (4)	Cu8—Cl1	2.4472 (14)	N11—C61	1.112 (8)
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
Cl5—Cu1—P1	115.48 (5)	Cl1—Cu8—N8	103.44 (14)	Cl2—Cu4—N4	103.37 (14)	Cu4—P3—Cu6	126.57 (5)
Cl5—Cu1—N1	103.04 (15)	Cl2—Cu8—P5	108.51 (5)	P2—Cu4—P3	50.68 (4)	Cu4—P3—P2	62.65 (4)

Cl5—Cu1—Cl5^{i}	104.88 (5)	Cl2—Cu8—N8	107.36 (12)	P2—Cu4—N4	110.54 (12)	Cu4—P3—C11	111.71 (16)
P1—Cu1—N1	111.48 (14)	P5—Cu8—N8	123.30 (14)	P3—Cu4—N4	105.61 (14)	Cu5—P3—Cu6	68.81 (4)
Cl5^{i}—Cu1—P1	115.25 (5)	Cl6—Cu9—Cl7	99.83 (6)	Cl1—Cu5—Cl3	101.05 (5)	Cu5—P3—P2	127.13 (6)
Cl5^{i}—Cu1—N1	105.50 (14)	Cl6—Cu9—P4	122.28 (6)	Cl1—Cu5—P3	109.88 (5)	Cu5—P3—C11	125.50 (14)
Cl4—Cu2—P2	108.70 (5)	Cl7—Cu9—P4	137.45 (6)	Cl1—Cu5—N5	105.60 (14)	Cu6—P3—P2	111.24 (6)
Cl4—Cu2—P6	115.22 (5)	Cl6—Cu10—Cl7	95.00 (6)	Cl3—Cu5—P3	115.49 (5)	Cu6—P3—C11	121.25 (16)
Cl4—Cu2—N2	104.35 (14)	Cl6—Cu10—Cl8	140.49 (7)	Cl3—Cu5—N5	106.79 (13)	P2—P3—C11	100.37 (14)
P2—Cu2—P6	106.52 (5)	Cl7—Cu10—Cl8	124.33 (7)	P3—Cu5—N5	116.52 (12)	Cu9—P4—C21	129.97 (16)
P2—Cu2—N2	106.79 (14)	Cu1—P1—C1	124.25 (14)	Cl3—Cu6—Cl4	110.07 (5)	Cu9—P4—C31	124.28 (15)
P6—Cu2—N2	114.89 (14)	Cu1—P1—C11	131.57 (17)	Cl3—Cu6—P3	106.50 (5)	C21—P4—C31	103.6 (2)
Cl2—Cu3—P2	105.08 (5)	C1—P1—C11	104.2 (2)	Cl3—Cu6—N6	96.35 (12)	Cu7—P5—Cu8	71.23 (5)
Cl2—Cu3—P6	108.66 (5)	Cu2—P2—Cu3	65.22 (4)	Cl4—Cu6—P3	108.52 (5)	Cu7—P5—P6	128.47 (7)
Cl2—Cu3—N3	109.71 (14)	Cu2—P2—Cu4	119.11 (5)	Cl4—Cu6—N6	115.85 (14)	Cu7—P5—C21	123.63 (13)
P2—Cu3—P6	106.69 (5)	Cu2—P2—P3	102.92 (6)	P3—Cu6—N6	118.30 (14)	Cu8—P5—P6	111.92 (6)
P2—Cu3—N3	114.90 (14)	Cu2—P2—C1	129.82 (16)	Cl1—Cu7—Cl3	92.82 (4)	Cu8—P5—C21	117.68 (17)
P6—Cu3—N3	111.46 (14)	Cu3—P2—Cu4	78.70 (4)	Cl1—Cu7—P5	102.58 (5)	P6—P5—C21	101.00 (14)
Cl1—Cu4—Cl2	92.76 (4)	Cu3—P2—P3	131.52 (6)	Cl1—Cu7—N7	99.03 (14)	Cu2—P6—Cu3	66.07 (4)
Cl1—Cu4—P2	138.01 (5)	Cu3—P2—C1	124.30 (16)	Cl3—Cu7—P5	118.94 (5)	Cu2—P6—P5	130.60 (6)
Cl1—Cu4—P3	100.61 (4)	Cu4—P2—P3	66.68 (5)	Cl3—Cu7—N7	111.98 (14)	Cu2—P6—C31	126.32 (15)
Cl1—Cu4—N4	106.39 (11)	Cu4—P2—C1	110.90 (16)	P5—Cu7—N7	122.83 (14)	Cu3—P6—P5	106.52 (6)
Cl2—Cu4—P2	97.47 (4)	P3—P2—C1	99.93 (15)	Cl1—Cu8—Cl2	96.30 (5)	Cu3—P6—C31	121.21 (14)
Cl2—Cu4—P3	142.96 (5)	Cu4—P3—Cu5	75.75 (4)	Cl1—Cu8—P5	114.46 (5)	P5—P6—C31	100.03 (14)

Symmetry code(s): (i) -*x*, -*y*+2, -*z*+1

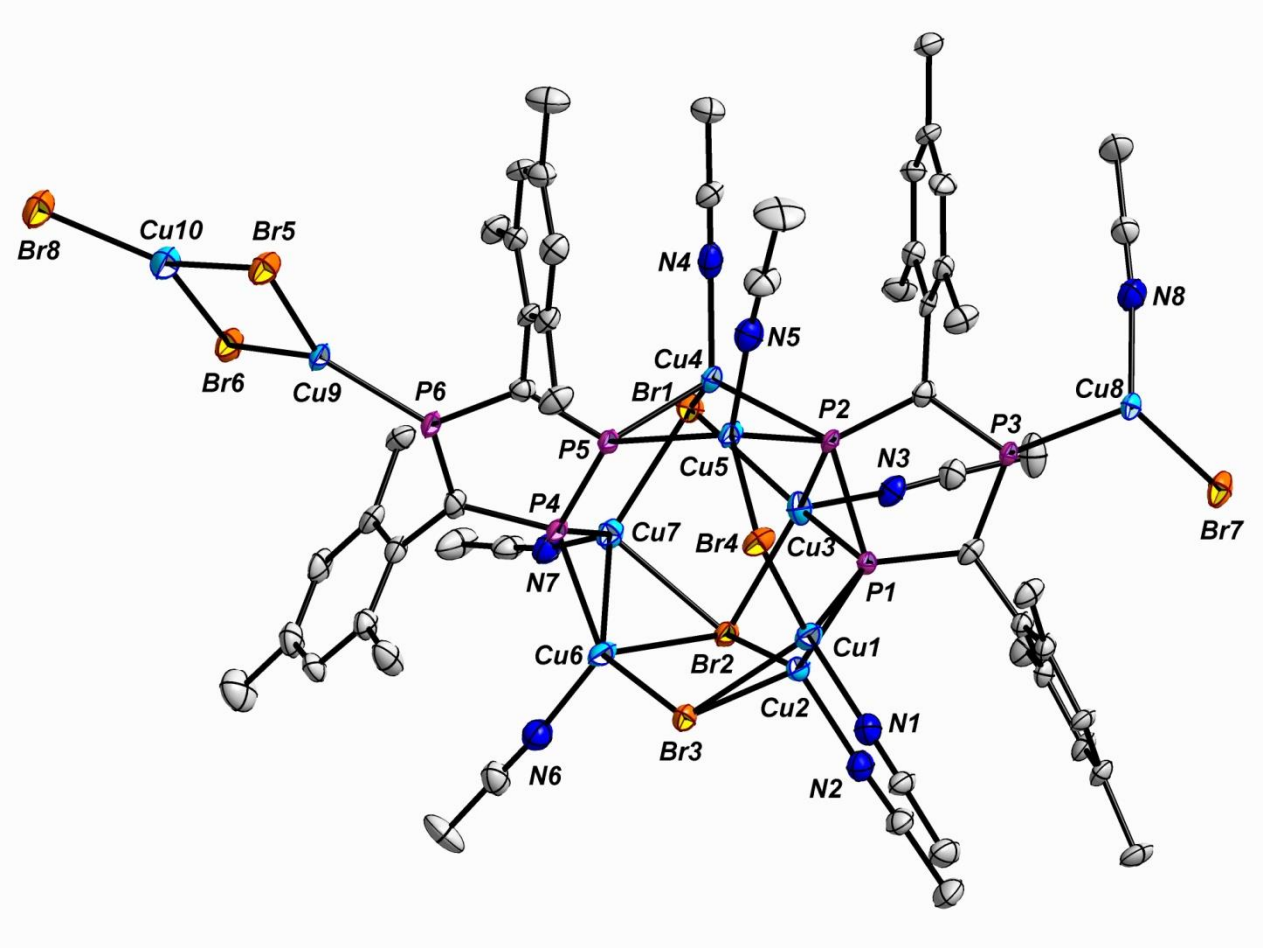


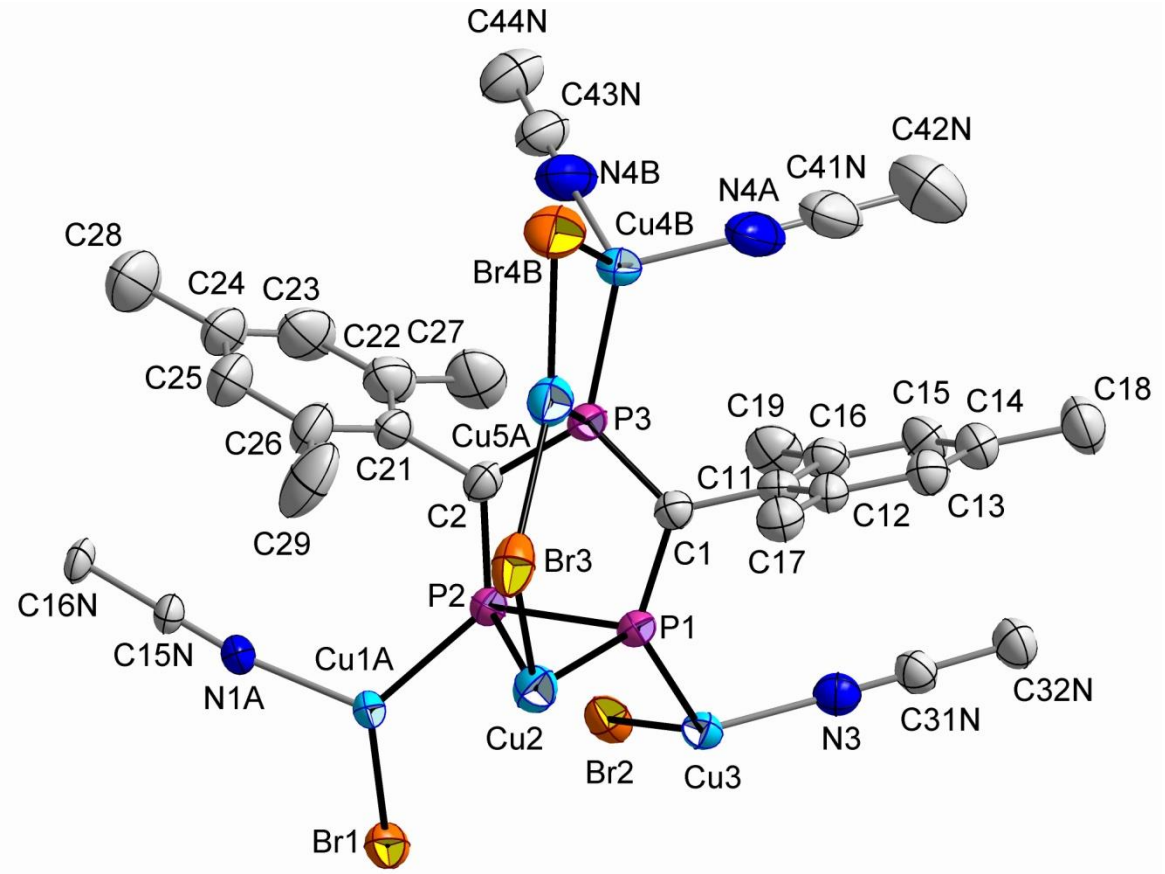
Fig. S 3. Independent part and numbering scheme in [{(Cu(MeCN))$_7$Br$_4$(P$_3$C$_2$(Mes)$_2$}$_2${Cu$_2$Br$_2$(MeCN)$_2$}{Cu$_2$Br$_3$}$_2$]·6MeCN (**3** · 6 CH$_3$CN). The hydrogen atoms are not shown.

Table S 5. Selected geometric parameters (Å, º) for **3** · 6 CH$_3$CN

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
Cu1-N1	1.974 (6)	Cu6-Br2	2.8521 (12)	Cu3-Cu4	2.9743 (13)	Cu10-Br8	2.2912 (12)
Cu1-P1	2.3093 (16)	Cu7-N7	1.972 (5)	Cu4-N4	1.987 (6)	Cu10-Br6	2.4143 (13)
Cu1-Br4	2.4266 (11)	Cu7-P4	2.2817 (17)	Cu4-P2	2.3086 (15)	Cu10-Br5	2.4368 (13)
Cu1-Cu2	2.5611 (13)	Cu7-Br1	2.5044 (11)	Cu4-P5	2.3793 (16)	Br7-Cu8^{i}	2.4852 (10)
Cu1-Br3	2.6599 (11)	Cu7-Br2	2.5580 (11)	Cu4-Br1	2.4718 (11)	P1-C1	1.738 (6)
Cu2-N2	1.971 (5)	Cu8-N8	2.011 (6)	Cu4-Cu5	2.5307 (12)	P1-P2	2.1125 (19)
Cu2-P1	2.2443 (15)	Cu8-P3	2.1887 (15)	Cu5-N5	1.990 (6)	P2-C2	1.748 (6)
Cu2-Br2	2.5049 (11)	Cu8-Br7	2.4673 (10)	Cu5-P5	2.2930 (15)	P3-C2	1.726 (6)
Cu2-Br3	2.5392 (11)	Cu8-Br7^{i}	2.4852 (10)	Cu5-P2	2.3864 (16)	P3-C1	1.741 (6)
Cu2-Cu3	2.9483 (13)	Cu8-Cu8^{i}	2.9262 (16)	Cu5-Br4	2.4536 (11)	P4-C3	1.750 (6)
Cu3-N3	2.021 (5)	Cu9-P6	2.1687 (16)	Cu6-N6	1.972 (6)	P4-P5	2.1007 (19)
Cu3-P2	2.4198 (16)	Cu9-Br5	2.3756 (11)	Cu6-P4	2.2298 (16)	P5-C4	1.739 (6)
Cu3-P1	2.5139 (17)	Cu9-Br6	2.3942 (10)	Cu6-Br3	2.4155 (11)	P6-C3	1.715 (6)
Cu3-Br2	2.5634 (11)	Cu9-Cu10	3.0074 (13)	Cu6-Cu7	2.5987 (13)	P6-C4	1.724 (6)
Cu3-Br1	2.6403 (11)						
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
N1-Cu1-P1	118.45 (16)	Cu7-Cu6-Br2	55.74 (3)	P5-Cu4-Br1	109.55 (5)	C2-P2-Cu3	110.5 (2)

N1-Cu1-Br4	114.86 (17)	N7-Cu7-P4	124.98 (17)	N5-Cu5-P5	115.26 (17)	P1-P2-Cu3	66.98 (6)
P1-Cu1-Br4	107.74 (5)	N7-Cu7-Br1	105.39 (17)	N5-Cu5-P2	108.66 (17)	Cu4-P2-Cu3	77.92 (5)
N1-Cu1-Br3	97.63 (16)	P4-Cu7-Br1	107.87 (5)	P5-Cu5-P2	106.34 (6)	Cu5-P2-Cu3	119.64 (6)
P1-Cu1-Br3	108.43 (5)	N7-Cu7-Br2	103.54 (16)	N5-Cu5-Br4	102.74 (17)	C2-P3-C1	104.2 (3)
Br4-Cu1-Br3	108.85 (4)	P4-Cu7-Br2	114.10 (5)	P5-Cu5-Br4	115.65 (5)	C2-P3-Cu8	123.5 (2)
N2-Cu2-P1	116.93 (16)	Br1-Cu7-Br2	97.21 (4)	P2-Cu5-Br4	107.89 (5)	C1-P3-Cu8	132.28 (19)
N2-Cu2-Br2	104.03 (16)	N8-Cu8-P3	111.74 (16)	N6-Cu6-P4	122.59 (18)	C3-P4-P5	100.5 (2)
P1-Cu2-Br2	111.29 (5)	N8-Cu8-Br7	106.46 (18)	N6-Cu6-Br3	110.51 (18)	C3-P4-Cu6	124.4 (2)
N2-Cu2-Br3	105.45 (16)	P3-Cu8-Br7	113.74 (5)	P4-Cu6-Br3	117.42 (6)	P5-P4-Cu6	128.31 (8)
P1-Cu2-Br3	114.95 (5)	N8-Cu8-Br7^{i}	103.59 (18)	C1-P1-Cu2	125.0 (2)	C3-P4-Cu7	116.3 (2)
Br2-Cu2-Br3	102.71 (3)	P3-Cu8-Br7^{i}	113.04 (5)	P2-P1-Cu2	127.32 (7)	P5-P4-Cu7	113.88 (8)
N3-Cu3-P2	108.75 (16)	Br7-Cu8-Br7^{i}	107.56 (3)	C1-P1-Cu1	121.0 (2)	Cu6-P4-Cu7	70.33 (5)
N3-Cu3-P1	103.42 (16)	P6-Cu9-Br5	134.04 (6)	P2-P1-Cu1	112.01 (7)	C4-P5-P4	99.8 (2)
P2-Cu3-P1	50.66 (5)	P6-Cu9-Br6	121.74 (6)	Cu2-P1-Cu1	68.43 (5)	C4-P5-Cu5	125.3 (2)
N3-Cu3-Br2	105.22 (16)	Br5-Cu9-Br6	103.64 (4)	C1-P1-Cu3	111.1 (2)	P4-P5-Cu5	132.11 (8)
P2-Cu3-Br2	139.92 (5)	Br8-Cu10-Br6	126.90 (5)	P2-P1-Cu3	62.36 (6)	C4-P5-Cu4	121.5 (2)
P1-Cu3-Br2	101.20 (5)	Br8-Cu10-Br5	131.57 (6)	Cu2-P1-Cu3	76.34 (5)	P4-P5-Cu4	106.31 (7)
N3-Cu3-Br1	102.10 (15)	Br6-Cu10-Br5	101.23 (4)	Cu1-P1-Cu3	127.32 (6)	Cu5-P5-Cu4	65.56 (5)
P2-Cu3-Br1	99.29 (5)	C1-P1-P2	100.6 (2)	C2-P2-P1	100.0 (2)	C3-P6-C4	104.4 (3)
P1-Cu3-Br1	145.71 (5)	N4-Cu4-P2	114.43 (15)	C2-P2-Cu4	123.2 (2)	C3-P6-Cu9	129.6 (2)
Br2-Cu3-Br1	93.74 (3)	N4-Cu4-P5	110.63 (16)	P1-P2-Cu4	131.91 (7)	C4-P6-Cu9	123.9 (2)
N6-Cu6-Br2	98.31 (18)	P2-Cu4-P5	106.07 (6)	C2-P2-Cu5	129.4 (2)		
P4-Cu6-Br2	105.55 (5)	N4-Cu4-Br1	108.45 (16)	P1-P2-Cu5	104.74 (7)		
Br3-Cu6-Br2	96.46 (4)	P2-Cu4-Br1	107.59 (5)	Cu4-P2-Cu5	65.21 (5)		

Symmetry code(s): (i) *-x*, *-y*, *-z*.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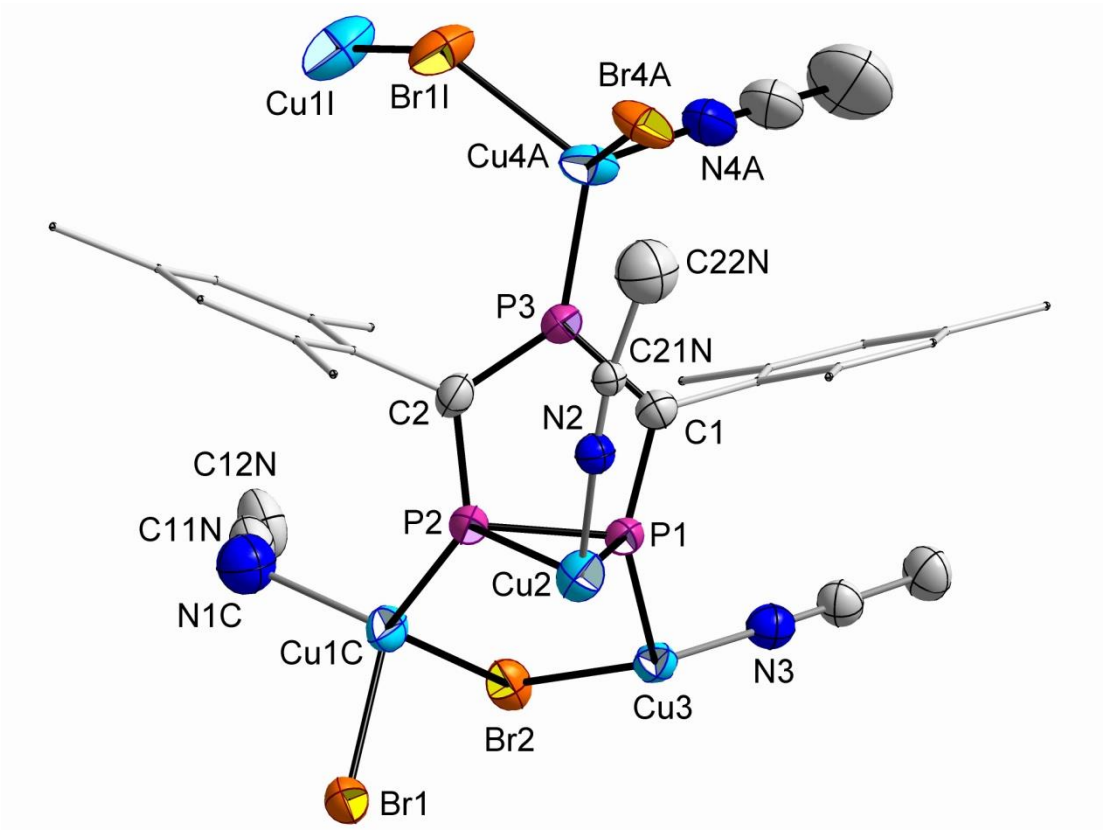
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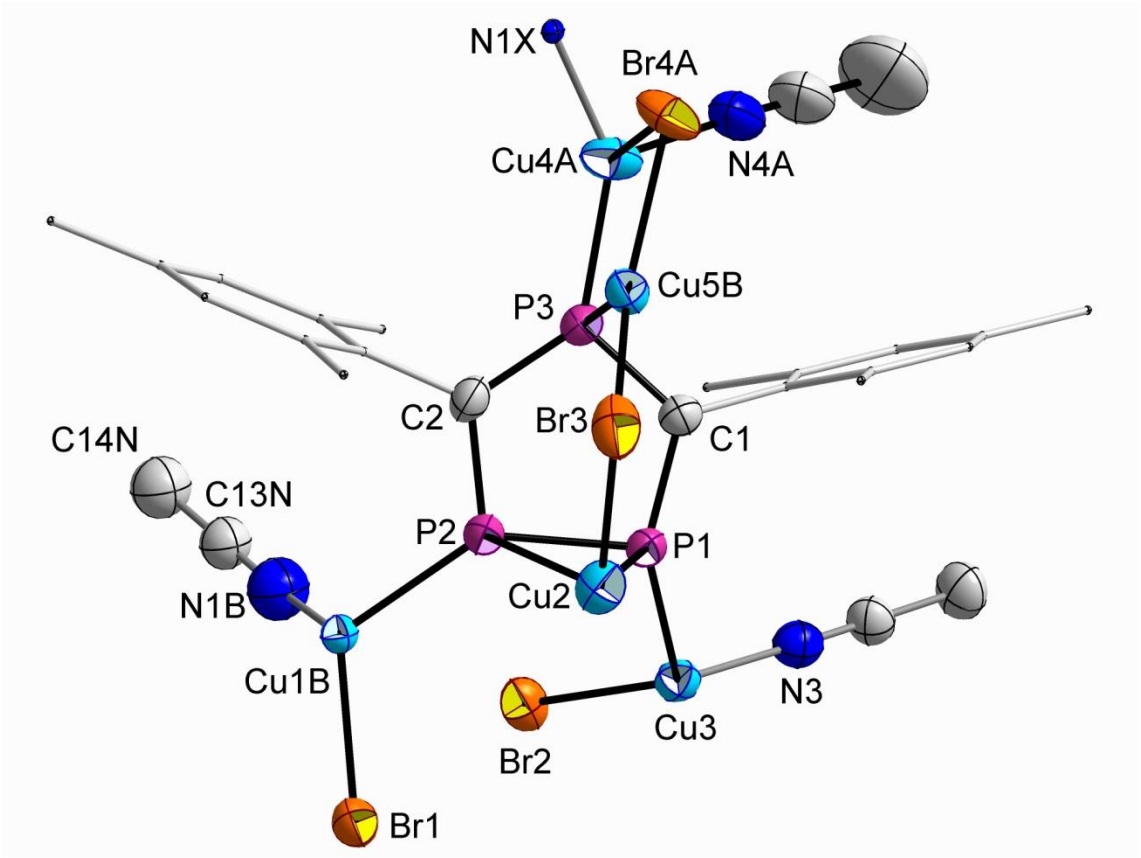
b



c

Fig. S 4. Independent part and numbering scheme in the disordered structure of **4** · CH_3CN: (a) major part, (b), and (c) minor parts. The hydrogen atoms and atoms belonging to other parts are not shown.

Table S 6. Selected geometric parameters (Å, º) for **4** · CH_3CN

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
Cu1A-N1A	1.998 (6)	Cu4B-P3	2.2192 (18)	Cu2-P1	2.4186 (14)	P2-C2	1.742 (5)
Cu1A-Br1	2.5111 (13)	N1X-Br4B	1.21 (4)	Cu2-P2	2.5207 (14)	P3-C1	1.721 (5)
Cu1A-Br1^{i}	2.5922 (13)	N1X-Br4C	0.70 (5)	Br2-Cu2^{i}	2.5542 (10)	P3-C2	1.734 (5)
Cu1A-P2	2.2018 (15)	Br4B-Br4C	0.670 (4)	Br2-Cu3	2.4305 (8)	C1-C11	1.489 (7)
N1A-C15N	1.128 (9)	Br3-N2	0.507 (13)	Cu4A-Cu5B	2.642 (8)	C11-C12	1.391 (7)
C15N-C16N	1.462 (8)	Br3-C21N	0.636 (12)	Cu4A-Br4A	2.516 (6)	C11-C16	1.412 (7)
Cu1B-N1B	2.07 (3)	Br3-C22N	2.17 (2)	Cu4A-Br1I	2.493 (6)	C12-C13	1.405 (8)
Cu1B-Br1	2.413 (6)	N2-C21N	1.063 (18)	Cu4A-N4A	2.298 (10)	C12-C17	1.494 (7)
Cu1B-P2	2.290 (6)	C21N-C22N	1.56 (3)	Cu4A-P3	2.189 (4)	C13-C14	1.387 (8)
N1B-C13N	1.26 (3)	N4A-C41N	1.140 (14)	Cu5B-Br4A	2.334 (8)	C14-C15	1.381 (9)
C13N-C14N	1.42 (3)	C41N-C42N	1.468 (19)	Cu5B-Br3	2.166 (7)	C14-C18	1.503 (9)
Cu1C-N1C	2.306 (16)	N4B-C43N	1.137 (13)	Cu5B-P3	2.551 (8)	C15-C16	1.395 (8)
Cu1C-Br1	2.540 (5)	C43N-C44N	1.454 (14)	Cu1I-Br1I	2.226 (4)	C16-C19	1.507 (8)
Cu1C-Br2	2.526 (5)	Cu3-Cu2^{i}	2.8535 (11)	Cu1I-Br1I^{ii}	2.226 (4)	C2-C21	1.485 (7)
Cu1C-P2	2.376 (4)	Cu3-Cu3^{i}	2.5325 (13)	Cu5A-Cu4B	2.861 (7)	C21-C22	1.391 (9)
N1C-C11N	1.40 (2)	Cu3-N3	1.987 (5)	Cu5A-Br4B	2.377 (8)	C21-C26	1.413 (9)
C11N-C12N	1.12 (2)	Cu3-P1^{i}	2.3211 (12)	Cu5A-Br3	2.552 (7)	C22-C23	1.374 (11)
Br1-Cu1A^{i}	2.5921 (13)	Cu3-P1	2.3543 (13)	Cu5A-P3	2.341 (8)	C22-C27	1.513 (12)
Br1-Cu2^{i}	2.5582 (11)	N3-C31N	1.150 (7)	Cu4B-N1X	2.30 (4)	C23-C24	1.416 (14)

Cu2-Br1^{i}	2.5582 (11)	C31N-C32N	1.444 (8)	Cu4B-Br4B	2.517 (5)	C24-C25	1.386 (12)
Cu2-Br2^{i}	2.5542 (10)	P1-Cu3^{i}	2.3211 (12)	Cu4B-Br4C	2.395 (3)	C24-C28	1.502 (10)
Cu2-Br3	2.519 (2)	P1-P2	2.1115 (17)	Cu4B-N4A	1.945 (8)	C25-C26	1.381 (9)
Cu2-Cu3^{i}	2.8535 (11)	P1-C1	1.752 (5)	Cu4B-N4B	2.080 (9)	C26-C29	1.468 (11)
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
N1A-Cu1A-Br1	106.18 (19)	N4A-Cu4A-Br4A	111.8 (3)	Cu1C-P2-Cu2	128.75 (11)	Cu4B-P3-Cu5B	85.21 (18)
N1A-Cu1A-Br1^{i}	111.8 (2)	N4A-Cu4A-Br1I	114.6 (3)	P1-P2-Cu1A	131.04 (7)	Cu4B-P3-Cu5A	77.66 (18)
N1A-Cu1A-P2	116.96 (18)	P3-Cu4A-Cu5B	62.9 (2)	P1-P2-Cu1B	135.24 (16)	C1-P3-Cu4A	123.0 (2)
Br1-Cu1A-Br1^{i}	103.89 (4)	Br1I-Cu4A-Br4A	94.1 (2)	P3-Cu4A-Br4A	116.6 (2)	C1-P3-Cu5B	92.8 (2)
P2-Cu1A-Br1	119.00 (6)	N4A-Cu4A-Cu5B	127.9 (3)	P3-Cu4A-Br1I	117.8 (2)	C1-P3-Cu5A	102.3 (2)
P2-Cu1A-Br1^{i}	97.98 (5)	N2-Br3-Cu5B	105.5 (14)	P3-Cu4A-N4A	102.6 (3)	C1-P3-Cu4B	123.17 (18)
C15N-N1A-Cu1A	172.3 (6)	N2-Br3-Cu5A	105.4 (14)	Br4A-Cu5B-Cu4A	60.4 (2)	C1-P3-C2	104.7 (2)
N1A-C15N-C16N	178.8 (8)	N2-Br3-C21N	136.7 (19)	Br4A-Cu5B-P3	110.1 (3)	C2-P3-Cu4A	129.6 (2)
N1B-Cu1B-Br1	105.5 (8)	N2-Br3-C22N	146.6 (16)	Br3-Cu5B-Cu4A	164.8 (4)	C2-P3-Cu5B	97.3 (3)
N1B-Cu1B-P2	109.7 (8)	C21N-Br3-Cu2	140.4 (11)	Br3-Cu5B-Br4A	134.3 (4)	C2-P3-Cu5A	97.5 (3)
P2-Cu1B-Br1	119.5 (3)	C21N-Br3-C22N	11.7 (12)	Br3-Cu5B-P3	115.6 (4)	C2-P3-Cu4B	131.96 (17)
C13N-N1B-Cu1B	163 (2)	C22N-Br3-Cu2	151.1 (6)	P3-Cu5B-Cu4A	49.83 (16)	P3-C1-P1	116.9 (3)
N1B-C13N-C14N	175 (3)	Br3-C21N-C22N	163.5 (17)	Cu5B-Br4A-Cu4A	65.9 (2)	C11-C1-P1	120.0 (3)
N1C-Cu1C-Br1	109.5 (4)	N2-C21N-C22N	171.1 (16)	Br1I-Cu1I-Br1I^{ii}	180.0	C11-C1-P3	122.3 (3)
N1C-Cu1C-Br2	108.6 (4)	Cu4B-N4A-Cu4A	16.18 (13)	Cu1I-Br1I-Cu4A	118.3 (2)	C12-C11-C1	121.9 (4)
N1C-Cu1C-P2	117.1 (4)	C41N-N4A-Cu4A	177.2 (7)	Br4B-Cu5A-Cu4B	56.55 (19)	C12-C11-C16	120.2 (5)
Br2-Cu1C-Br1	98.00 (13)	C41N-N4A-Cu4B	165.3 (9)	Br4B-Cu5A-Br3	145.3 (4)	C16-C11-C1	117.9 (4)
P2-Cu1C-Br1	111.48 (17)	N4A-C41N-C42N	178.7 (17)	Br3-Cu5A-Cu4B	158.0 (3)	C11-C12-C13	118.6 (5)
P2-Cu1C-Br2	110.57 (16)	C43N-N4B-Cu4B	174.3 (10)	P3-Cu5A-Br4B	105.1 (3)	C11-C12-C17	121.8 (5)
C11N-N1C-Cu1C	117.6 (11)	N4B-C43N-C44N	179.9 (16)	P3-Cu5A-Br3	109.5 (3)	C13-C12-C17	119.6 (5)
C12N-C11N-N1C	175.5 (16)	Br2-Cu3-Cu3^{i}	151.00 (2)	Br4B-Cu4B-Cu5A	51.98 (18)	C14-C13-C12	122.3 (5)
Cu1A-Br1-Cu1A^{i}	75.82 (4)	Cu3^{i}-Cu3-Cu2^{i}	101.42 (3)	Br4C-Cu4B-Cu5A	67.3 (2)	C13-C14-C18	122.5 (6)
Cu1A-Br1-Cu2^{i}	105.63 (4)	N3-Cu3-Cu2^{i}	137.31 (13)	N4A-Cu4B-Cu5A	120.5 (3)	C15-C14-C13	117.8 (5)
Cu1B-Br1-Cu1A^{i}	103.68 (14)	N3-Cu3-Br2	108.07 (13)	N4A-Cu4B-N1X	112.9 (11)	C15-C14-C18	119.7 (6)
Cu1B-Br1-Cu2^{i}	103.80 (15)	N3-Cu3-Cu3^{i}	100.91 (12)	N4A-Cu4B-Br4B	110.0 (3)	C14-C15-C16	122.3 (5)
Cu1C-Br1-Cu1A^{i}	114.50 (9)	N3-Cu3-P1^{i}	111.84 (13)	N4A-Cu4B-Br4C	104.4 (3)	C11-C16-C19	122.0 (5)
Cu1C-Br1-Cu2^{i}	77.19 (10)	N3-Cu3-P1	111.04 (13)	N4A-Cu4B-N4B	99.8 (4)	C15-C16-C11	118.7 (5)
Cu2^{i}-Br1-Cu1A^{i}	80.52 (3)	P1-Cu3-Cu2^{i}	111.63 (4)	N4A-Cu4B-P3	114.3 (2)	C15-C16-C19	119.3 (5)
Br1^{i}-Cu2-Cu3^{i}	120.41 (4)	P1^{i}-Cu3-Br2	110.35 (4)	N4B-Cu4B-Cu5A	139.6 (3)	P3-C2-P2	117.8 (3)
Br2^{i}-Cu2-Br1^{i}	96.81 (3)	P1-Cu3-Br2	109.88 (4)	N4B-Cu4B-N1X	86.9 (12)	C21-C2-P2	119.8 (4)
Br2^{i}-Cu2-Cu3^{i}	53.07 (2)	P1^{i}-Cu3-Cu3^{i}	57.84 (4)	N4B-Cu4B-Br4B	115.0 (3)	C21-C2-P3	122.0 (4)
Br3-Cu2-Br1^{i}	107.88 (5)	P1-Cu3-Cu3^{i}	56.57 (4)	N4B-Cu4B-Br4C	103.0 (3)	C22-C21-C2	119.3 (6)
Br3-Cu2-Br2^{i}	101.14 (4)	P1^{i}-Cu3-P1	105.65 (5)	N4B-Cu4B-P3	113.7 (3)	C22-C21-C26	118.7 (6)
Br3-Cu2-Cu3^{i}	126.01 (5)	C31N-N3-Cu3	175.7 (4)	P3-Cu4B-Cu5A	53.07 (16)	C26-C21-C2	122.0 (5)
Br3-Cu2-P2	105.91 (5)	N3-C31N-C32N	179.3 (6)	P3-Cu4B-N1X	123.2 (9)	C21-C22-C27	120.0 (6)
P1-Cu2-Br1^{i}	130.89 (5)	Cu3^{i}-P1-Cu2	74.00 (4)	P3-Cu4B-Br4B	104.31 (13)	C23-C22-C21	120.6 (8)
P1-Cu2-Br2^{i}	103.32 (4)	Cu3-P1-Cu2	121.95 (5)	P3-Cu4B-Br4C	119.18 (14)	C23-C22-C27	119.4 (7)
P1-Cu2-Br3	111.33 (6)	Cu3^{i}-P1-Cu3	65.59 (4)	Cu5A-Br4B-Cu4B	71.5 (2)	C22-C23-C24	121.5 (7)
P1-Cu2-Cu3^{i}	51.44 (3)	P2-P1-Cu2	67.22 (5)	Cu2-Br3-Cu5A	106.64 (18)	C23-C24-C28	121.5 (8)

P1-Cu2-P2	50.56 (4)	P2-P1-Cu3^{i}	129.44 (7)	Cu5B-Br3-Cu2	107.4 (2)	C25-C24-C23	117.2 (6)
P2-Cu2-Br1^{i}	91.13 (4)	P2-P1-Cu3	110.02 (6)	P1-P2-Cu1C	106.93 (12)	C25-C24-C28	121.2 (9)
P2-Cu2-Br2^{i}	147.88 (5)	C1-P1-Cu2	111.07 (16)	P1-P2-Cu2	62.21 (5)	C26-C25-C24	122.1 (8)
P2-Cu2-Cu3^{i}	96.29 (4)	C1-P1-Cu3^{i}	123.08 (16)	C2-P2-Cu1A	128.61 (18)	C21-C26-C29	122.3 (6)
Cu1C-Br2-Cu2^{i}	77.52 (10)	C1-P1-Cu3	125.45 (17)	C2-P2-Cu1B	117.0 (2)	C25-C26-C21	119.9 (7)
Cu3-Br2-Cu1C	93.95 (8)	C1-P1-P2	100.87 (17)	C2-P2-Cu1C	119.7 (2)	C25-C26-C29	117.8 (7)
Cu3-Br2-Cu2^{i}	69.79 (3)	Cu1A-P2-Cu2	89.37 (5)	C2-P2-Cu2	111.56 (17)		
Br1I-Cu4A-Cu5B	116.1 (3)	Cu1B-P2-Cu2	119.47 (15)	C2-P2-P1	99.68 (17)		

Symmetry code(s): (i) -*x*+1, *y*, -*z*+1/2; (ii) -*x*+3/2, -*y*+1/2, -*z*.

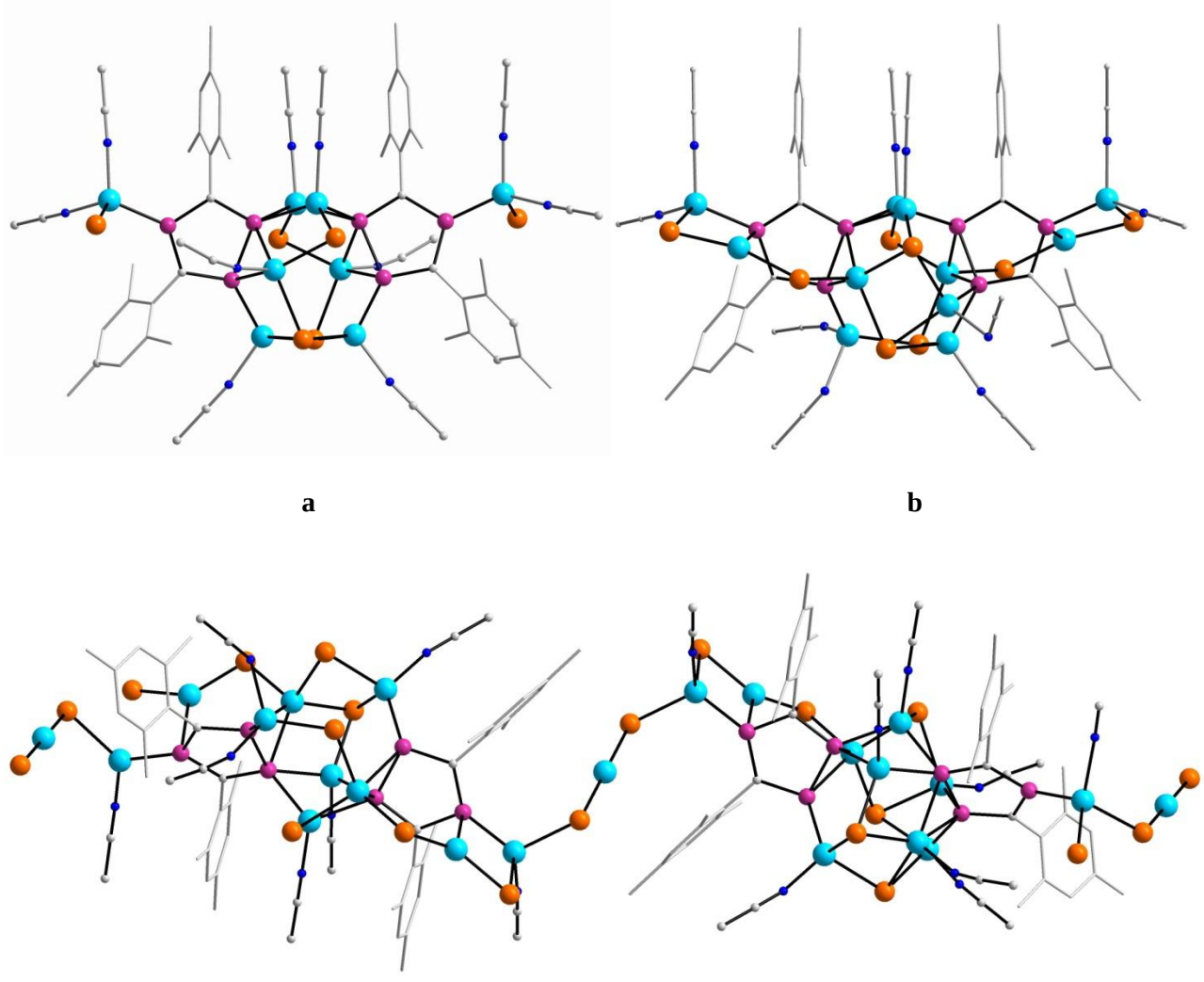


Fig. S 5. Some possible structural fragments in the solid solution of **4** · CH_3CN, a simplified view: (a) an oligomer (~70%), (b) an oligomer (~20%), and (c) a polymer (~10%). The hydrogen atoms and atoms belonging to other parts are not shown.

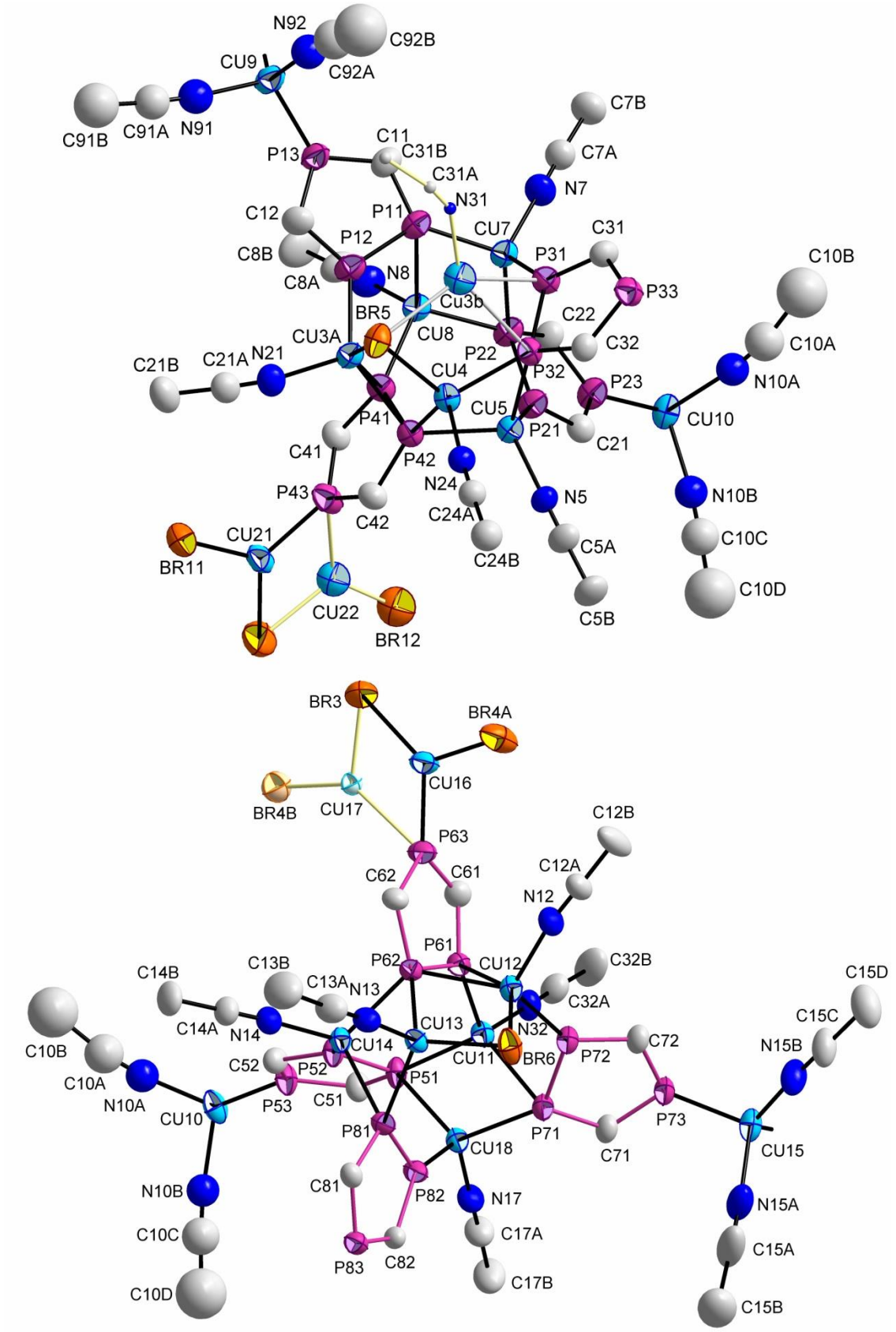


Fig. S 6. Independent part and numbering scheme in **5** · 2 CH_3CN. The mesityl ligands are omitted for clarity.

Table S 7. Selected geometric parameters (Å, º) for **5** · 2 CH_3CN

Bond	Distance, Å	Bond	Distance, Å
Cu1A—Br1A	2.245 (9)	Cu10—P23	2.231 (3)
Cu1A—Br2A	2.223 (11)	Cu10—P53	2.230 (2)
Cu2A—Br1A	2.144 (9)	Cu11—P51	2.315 (2)
Cu2A—Br3A	2.218 (12)	Cu11—P61	2.301 (2)
Br2—Cu21	2.350 (2)	Cu11—P71	2.509 (2)
Br2—Cu22	2.295 (13)	Cu12—Cu13	2.8718 (17)
Br5—Cu3A	2.5138 (17)	Cu12—P61	2.538 (2)
Br5—Cu3B	2.61 (2)	Cu12—P62	2.469 (2)
Br5—Cu4	2.4249 (17)	Cu12—P72	2.282 (2)
Cu21—Br11	2.395 (3)	Cu13—Cu14	2.5353 (16)
Cu21—P43	2.180 (3)	Cu13—P62	2.331 (2)
Cu22—Br12	2.313 (19)	Cu13—P81	2.326 (2)
Cu22—P43	2.514 (14)	Cu14—P52	2.239 (2)
Cu3A—Cu4	2.8637 (19)	Cu14—P62	2.398 (2)
Cu3A—P12	2.276 (3)	Cu14—P81	2.394 (2)
Cu3A—P41	2.545 (3)	Cu15—P73	2.233 (2)
Cu3A—P42	2.462 (3)	Cu15—P83^{ii}	2.252 (3)
Cu3B—Cu4	2.902 (19)	Cu16—Br4A	2.380 (2)
Cu3B—P31	2.81 (2)	Cu16—Br3	2.347 (2)
Cu3B—P32	2.54 (2)	Cu16—P63	2.178 (2)
Cu4—Cu5	2.5272 (18)	Cu17—Br4B	2.38 (3)
Cu4—P32	2.323 (3)	Cu17—Br3	2.24 (2)
Cu4—P42	2.316 (2)	Cu17—P63	2.56 (2)
Cu5—P21	2.231 (2)	Cu18—P51	2.373 (3)
Cu5—P32	2.396 (3)	Cu18—P71	2.282 (2)
Cu5—P42	2.402 (3)	Cu18—P82	2.266 (3)
Cu7—Cu8	2.6628 (19)	P11—P12	2.068 (4)
Cu7—P11	2.287 (3)	P21—P22	2.085 (3)
Cu7—P22	2.357 (3)	P31—P32	2.097 (3)
Cu7—P31	2.268 (2)	P41—P42	2.103 (3)
Cu8—P11	2.510 (3)	P51—P52	2.079 (3)
Cu8—P22	2.325 (3)	P61—P62	2.104 (3)
Cu8—P41	2.301 (2)	P71—P72	2.084 (3)
Cu9—P13	2.221 (3)	P81—P82	2.088 (3)
Cu9—P33^{i}	2.233 (3)		

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

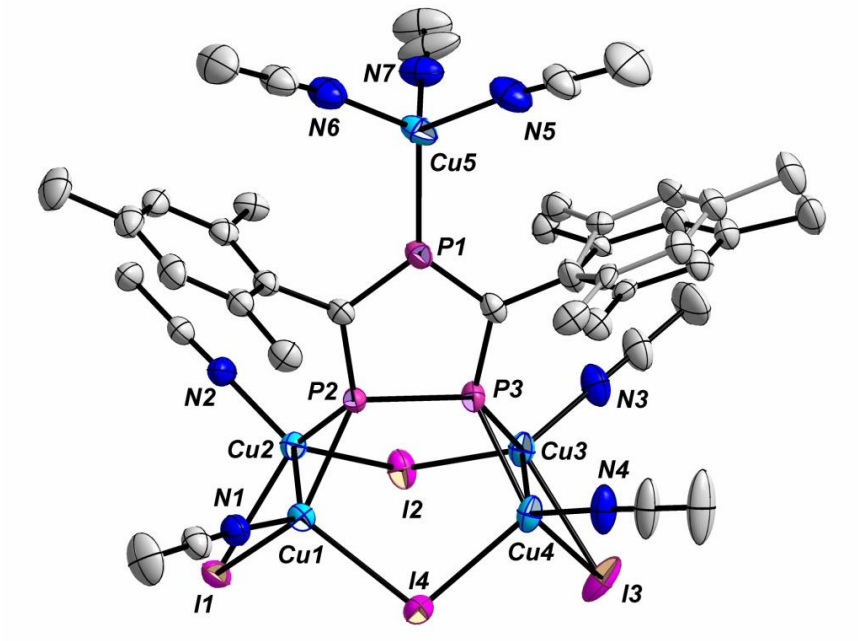


Fig. S 7. Independent part and numbering scheme in **6** · 0.5 C_7H_8 · 2.5 CH_3CN. The disordered mesityl ring is shown by lighter colour.

Table S 8. Selected geometric parameters (Å, º) for **6** · 0.5 C_7H_8 · 2.5 CH_3CN

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
C1-P1	1.722 (3)	Cu1-Cu2	2.5556 (7)	P2-P3	2.1047 (11)	Cu3-Cu4	2.5606 (7)
C1-P2	1.744 (3)	Cu1-I4	2.6515 (5)	P2-Cu1	2.2918 (9)	Cu3-I2	2.6330 (5)
C11-P1	1.727 (4)	Cu1-I1	2.6558 (5)	P2-Cu2	2.3348 (9)	Cu3-I3	2.6941 (6)
C11-P3	1.737 (3)	Cu2-I1	2.6433 (5)	P3-Cu3	2.3079 (9)	Cu4-I4	2.6493 (6)
P1-Cu5	2.2168 (10)	Cu2-I2	2.6671 (5)	P3-Cu4	2.3133 (10)	Cu4-I3	2.6563 (5)
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
P1-C1-P2	118.10 (19)	P2-Cu2-I2	106.18 (3)	N1-Cu1-P2	117.00 (9)	P3-Cu4-I4	106.40 (3)
P1-C11-P3	117.77 (18)	Cu1-Cu2-I2	118.72 (2)	N1-Cu1-Cu2	136.44 (9)	Cu3-Cu4-I4	116.10 (2)
C1-P1-C11	103.90 (15)	I1-Cu2-I2	108.048 (18)	P2-Cu1-Cu2	57.28 (2)	N4-Cu4-I3	106.21 (10)
C1-P1-Cu5	126.97 (12)	N3-Cu3-P3	116.08 (10)	N1-Cu1-I4	105.84 (9)	P3-Cu4-I3	118.14 (3)
C11-P1-Cu5	126.28 (11)	N3-Cu3-Cu4	131.81 (10)	P2-Cu1-I4	104.56 (3)	Cu3-Cu4-I3	62.153 (16)
C1-P2-P3	99.79 (11)	P3-Cu3-Cu4	56.45 (3)	Cu2-Cu1-I4	117.50 (2)	I4-Cu4-I3	104.40 (2)
C1-P2-Cu1	132.86 (11)	N3-Cu3-I2	107.79 (10)	N1-Cu1-I1	102.68 (9)	N5-Cu5-N6	108.18 (15)
P3-P2-Cu1	116.60 (4)	P3-Cu3-I2	104.10 (3)	P2-Cu1-I1	117.89 (3)	N5-Cu5-N7	104.12 (16)
C1-P2-Cu2	127.09 (11)	Cu4-Cu3-I2	120.32 (2)	Cu2-Cu1-I1	60.921 (16)	N6-Cu5-N7	106.15 (15)
P3-P2-Cu2	111.58 (4)	N3-Cu3-I3	100.64 (11)	I4-Cu1-I1	108.121 (18)	N5-Cu5-P1	112.92 (12)
Cu1-P2-Cu2	67.05 (3)	P3-Cu3-I3	116.86 (3)	N2-Cu2-P2	112.96 (9)	N6-Cu5-P1	113.70 (10)
C11-P3-P2	100.42 (12)	Cu4-Cu3-I3	60.667 (16)	N2-Cu2-Cu1	134.91 (10)	N7-Cu5-P1	111.12 (10)
C11-P3-Cu3	127.26 (11)	I2-Cu3-I3	111.29 (2)	P2-Cu2-Cu1	55.67 (2)	Cu2-I1-Cu1	57.668 (15)
P2-P3-Cu3	117.35 (4)	N4-Cu4-P3	111.22 (12)	N2-Cu2-I1	105.98 (9)	Cu3-I2-Cu2	99.059 (16)
C11-P3-Cu4	130.81 (12)	N4-Cu4-Cu3	133.73 (10)	P2-Cu2-I1	116.78 (3)	Cu4-I3-Cu3	57.179 (15)
P2-P3-Cu4	112.61 (4)	P3-Cu4-Cu3	56.25 (2)	Cu1-Cu2-I1	61.411 (16)	Cu4-I4-Cu1	98.954 (16)
Cu3-P3-Cu4	67.30 (3)	N4-Cu4-I4	110.16 (10)	N2-Cu2-I2	106.37 (10)		

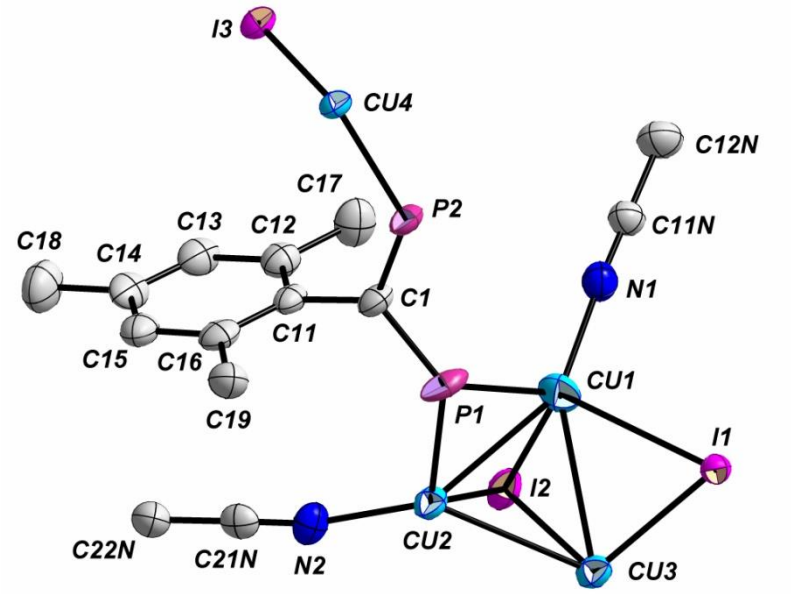


Fig. S 8. Independent part and numbering scheme in **7** · 2 C_7H_8.

Table S 9. Selected geometric parameters (Å, º) for **7** · 2 C_7H_8

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
I1-Cu1	2.8643 (16)	Cu2-I1^{i}	2.6691 (12)	I3-Cu3^{ii}	2.6026 (12)	Cu4-I3^{i}	2.5151 (9)
I1-Cu2^{i}	2.6690 (12)	Cu2-Cu3	2.8310 (15)	I3-Cu4	2.5152 (9)	Cu4-P2	2.191 (3)
I1-Cu3^{i}	2.6733 (12)	Cu2-P1	2.235 (2)	Cu1-Cu2	2.6883 (18)	P1-P1^{i}	2.077 (5)
I1-Cu3	2.6776 (13)	Cu2-N2	1.969 (8)	Cu1-Cu3	2.8639 (18)	P1-C1	1.727 (7)
I2-Cu1	2.6572 (19)	Cu3-I1^{i}	2.6734 (12)	Cu1-P1	2.428 (3)	P2-C1	1.715 (8)
I2-Cu2	2.6595 (13)	Cu3-I3^{iii}	2.6026 (12)	Cu1-N1	1.965 (8)	P2-C1^{i}	1.715 (8)
I2-Cu3	2.7088 (13)	Cu3-Cu3^{i}	2.876 (2)				
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
I2-Cu1-I1	105.43 (6)	I1^{i}-Cu3-I2	112.59 (4)	I1^{i}-Cu2-Cu3	58.07 (3)	I3^{iii}-Cu3-Cu2	140.99 (6)
I2-Cu1-Cu2	59.67 (4)	I1-Cu3-I2	109.36 (4)	I2-Cu2-I1^{i}	114.33 (4)	I3^{iii}-Cu3-Cu3^{i}	106.23 (3)
I2-Cu1-Cu3	58.62 (4)	I1^{i}-Cu3-Cu1	99.46 (5)	I2-Cu2-Cu1	59.58 (5)	I3^{i}-Cu4-I3	119.69 (6)
Cu2-Cu1-I1	109.84 (5)	I1-Cu3-Cu1	62.14 (4)	I2-Cu2-Cu3	59.02 (3)	P2-Cu4-I3^{i}	120.16 (3)
Cu3-Cu1-I1	55.74 (4)	I1^{i}-Cu3-Cu2	57.93 (3)	P1-Cu2-I1^{i}	103.13 (7)	P2-Cu4-I3	120.16 (3)
P1-Cu1-I1	117.82 (8)	I1-Cu3-Cu2	111.16 (5)	P1-Cu2-I2	112.75 (8)	Cu2-P1-Cu1	70.28 (7)
P1-Cu1-I2	106.69 (8)	I1^{i}-Cu3-Cu3^{i}	57.56 (4)	P1-Cu2-Cu1	58.24 (8)	P1^{i}-P1-Cu1	79.64 (13)
P1-Cu1-Cu2	51.49 (6)	I1-Cu3-Cu3^{i}	57.41 (4)	P1-Cu2-Cu3	108.75 (8)	P1^{i}-P1-Cu2	130.02 (7)
P1-Cu1-Cu3	102.36 (7)	I2-Cu3-Cu1	56.87 (4)	N2-Cu2-I1^{i}	112.8 (2)	C1-P1-Cu1	125.1 (3)
N1-Cu1-I1	100.7 (2)	I2-Cu3-Cu2	57.33 (3)	N2-Cu2-I2	103.2 (2)	C1-P1-Cu2	129.3 (3)
N1-Cu1-I2	112.1 (2)	I2-Cu3-Cu3^{i}	150.10 (3)	N2-Cu2-Cu1	143.0 (2)	C1-P1-P1^{i}	100.6 (3)
N1-Cu1-Cu2	149.4 (2)	I3^{iii}-Cu3-I1^{i}	114.90 (4)	N2-Cu2-Cu3	140.3 (2)	C1-P2-Cu4	127.7 (3)
N1-Cu1-Cu3	143.5 (2)	I3^{iii}-Cu3-I1	107.22 (4)	N2-Cu2-P1	110.9 (2)	C1^{i}-P2-Cu4	127.7 (3)
N1-Cu1-P1	113.9 (2)	I3^{iii}-Cu3-I2	103.37 (4)	I1^{i}-Cu3-I1	109.11 (4)	C1-P2-C1^{i}	104.6 (5)
I1^{i}-Cu2-Cu1	104.17 (5)	I3^{iii}-Cu3-Cu1	145.41 (6)				

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

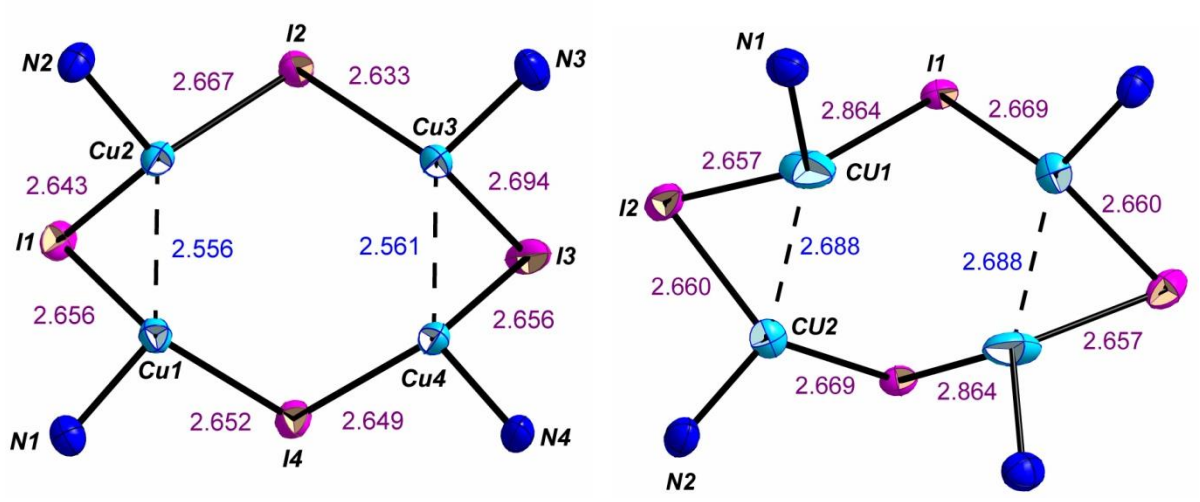


Fig. S 9. The geometry of the Cu_4I_4 'crown' fragment in comparison for (a) **6** · 0.5 C_7H_8 · 2.5 CH_3CN and (b) **7** · 2 C_7H_8**.**

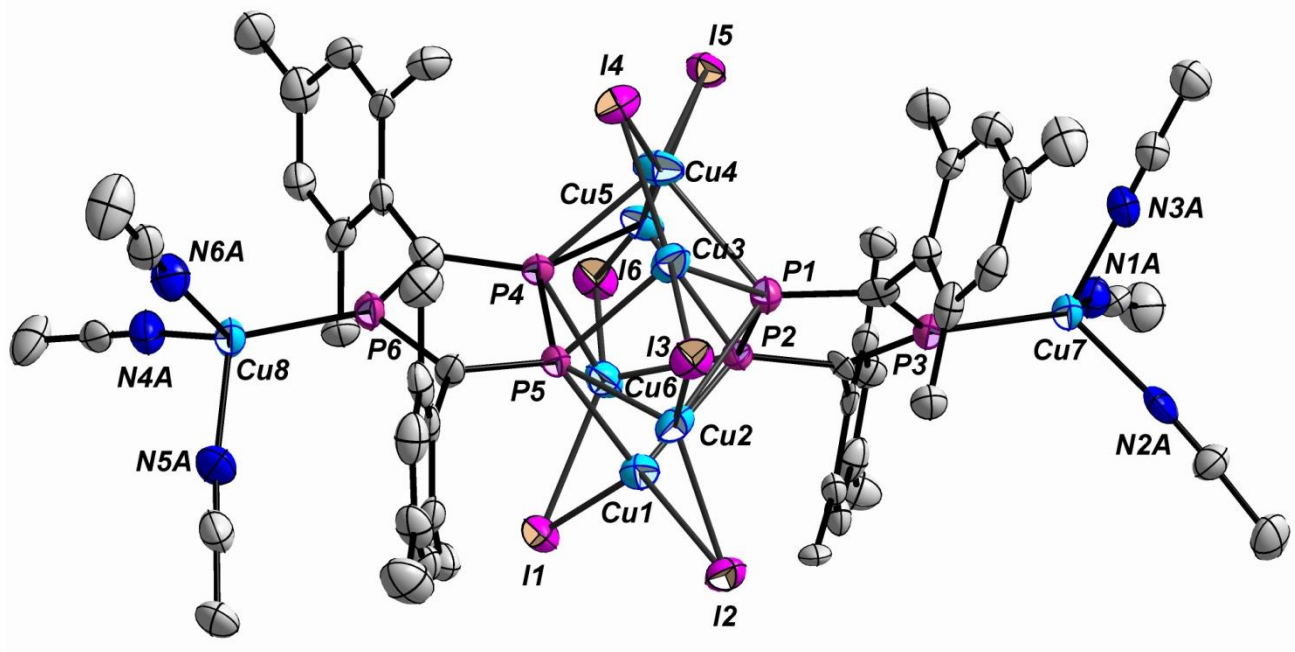


Fig. S 10. Independent part and numbering scheme in **8** · 0.5 CH_2Cl_2 · 3 CH_3CN. The hydrogen atoms are not shown.

Table S 10. Selected geometric parameters (Å, º) for **8** · 0.5 CH_2Cl_2 · 3 CH_3CN

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
Cu1-Cu2	2.553 (3)	Cu5-P2	2.624 (4)	Cu3-I3	2.584 (2)	Cu8-N5A	2.034 (14)
Cu1-Cu6	2.516 (3)	Cu5-P4	2.331 (4)	Cu3-I4	2.562 (2)	Cu8-N6A	2.012 (14)
Cu1-I1	2.627 (2)	Cu6-I1	2.555 (2)	Cu3-P1	2.306 (4)	P1-P2	2.124 (5)
Cu1-I2	2.590 (2)	Cu6-I6	2.599 (2)	Cu3-P5	2.650 (4)	P1-C1	1.727 (14)
Cu1-P2	2.511 (4)	Cu6-P2	2.341 (4)	Cu4-Cu5	2.494 (3)	P2-C2	1.730 (12)
Cu1-P5	2.522 (4)	Cu6-P4	2.646 (4)	Cu4-I4	2.563 (2)	P3-C1	1.720 (15)
Cu2-Cu3	2.483 (3)	Cu7-P3	2.218 (4)	Cu4-I5	2.585 (2)	P3-C2	1.754 (13)
Cu2-I2	2.550 (2)	Cu7-N1A	1.983 (13)	Cu4-P1	2.570 (4)	P4-P5	2.122 (5)
Cu2-I3	2.586 (2)	Cu7-N2A	2.049 (14)	Cu4-P4	2.543 (4)	P4-C4	1.724 (13)
Cu2-P1	2.820 (4)	Cu7-N3A	2.033 (14)	Cu5-Cu6	2.471 (3)	P5-C3	1.719 (13)
Cu2-P5	2.304 (4)	Cu8-P6	2.202 (4)	Cu5-I5	2.564 (2)	P6-C3	1.734 (13)
Cu3-Cu4	2.537 (3)	Cu8-N4A	1.994 (15)	Cu5-I6	2.587 (2)	P6-C4	1.720 (13)
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
I2-Cu1-I1	121.75 (8)	Cu3-P1-Cu4	62.42 (10)	I5-Cu5-P2	116.33 (10)	P5-P4-Cu4	94.39 (16)
P2-Cu1-I1	109.36 (11)	Cu4-P1-Cu2	106.46 (12)	I6-Cu5-P2	100.84 (10)	P5-P4-Cu5	127.31 (18)
P2-Cu1-I2	110.81 (11)	P2-P1-Cu2	92.74 (15)	P4-Cu5-I5	116.72 (12)	P5-P4-Cu6	92.21 (15)
P2-Cu1-P5	91.38 (12)	P2-P1-Cu3	127.78 (17)	P4-Cu5-I6	107.90 (11)	C4-P4-Cu4	127.8 (5)
P5-Cu1-I1	109.83 (11)	P2-P1-Cu4	93.82 (15)	P4-Cu5-P2	86.21 (12)	C4-P4-Cu5	132.6 (5)
P5-Cu1-I2	109.50 (11)	C1-P1-Cu2	123.1 (4)	I1-Cu6-I6	123.67 (8)	C4-P4-Cu6	120.6 (4)
I2-Cu2-I3	127.23 (8)	C1-P1-Cu3	132.6 (5)	I1-Cu6-P4	114.49 (11)	C4-P4-P5	99.7 (5)
I2-Cu2-P1	108.55 (10)	C1-P1-Cu4	127.6 (4)	I6-Cu6-P4	98.68 (10)	Cu1-P5-Cu3	107.79 (13)
I3-Cu2-P1	98.54 (10)	C1-P1-P2	99.2 (5)	P2-Cu6-I1	117.74 (12)	Cu2-P5-Cu1	63.68 (10)
P5-Cu2-I2	118.56 (12)	Cu1-P2-Cu5	109.46 (13)	P2-Cu6-I6	108.65 (11)	Cu2-P5-Cu3	59.66 (10)
P5-Cu2-I3	109.02 (12)	Cu6-P2-Cu1	62.36 (10)	P2-Cu6-P4	85.49 (12)	P4-P5-Cu1	96.07 (16)
P5-Cu2-P1	82.56 (12)	Cu6-P2-Cu5	59.37 (10)	N1A-Cu7-P3	117.1 (3)	P4-P5-Cu2	135.07 (18)
I3-Cu3-P5	99.17 (10)	P1-P2-Cu1	96.03 (16)	N1A-Cu7-N2A	96.9 (5)	P4-P5-Cu3	94.30 (15)
I4-Cu3-I3	120.56 (9)	P1-P2-Cu5	93.72 (15)	N1A-Cu7-N3A	104.1 (5)	C3-P5-Cu1	126.6 (5)
I4-Cu3-P5	111.57 (10)	P1-P2-Cu6	130.89 (18)	N2A-Cu7-P3	122.1 (3)	C3-P5-Cu2	124.6 (5)
P1-Cu3-I3	113.80 (12)	C2-P2-Cu1	128.5 (4)	N3A-Cu7-P3	113.5 (3)	C3-P5-Cu3	121.2 (5)
P1-Cu3-I4	117.60 (12)	C2-P2-Cu5	117.3 (4)	N3A-Cu7-N2A	100.1 (5)	C3-P5-P4	99.9 (5)
P1-Cu3-P5	86.42 (13)	C2-P2-Cu6	127.4 (5)	N4A-Cu8-P6	119.2 (4)	C3-P6-Cu8	120.9 (4)
I4-Cu4-I5	121.85 (9)	C2-P2-P1	101.0 (5)	N4A-Cu8-N5A	100.3 (6)	C4-P6-Cu8	134.4 (5)
I4-Cu4-P1	108.50 (11)	C1-P3-Cu7	126.2 (5)	N4A-Cu8-N6A	106.1 (5)	C4-P6-C3	103.3 (6)
P1-Cu4-I5	111.56 (11)	C1-P3-C2	103.6 (6)	N5A-Cu8-P6	109.0 (4)	P3-C1-P1	119.3 (8)
P4-Cu4-I4	109.52 (11)	C2-P3-Cu7	128.7 (4)	N6A-Cu8-P6	118.4 (4)	P2-C2-P3	116.9 (8)
P4-Cu4-I5	108.77 (11)	Cu4-P4-Cu6	108.63 (13)	N6A-Cu8-N5A	100.9 (5)	P5-C3-P6	118.4 (8)
P4-Cu4-P1	92.74 (12)	Cu5-P4-Cu4	61.36 (10)	Cu3-P1-Cu2	56.89 (10)	P6-C4-P4	118.7 (8)
I5-Cu5-I6	122.21 (8)	Cu5-P4-Cu6	59.13 (10)				

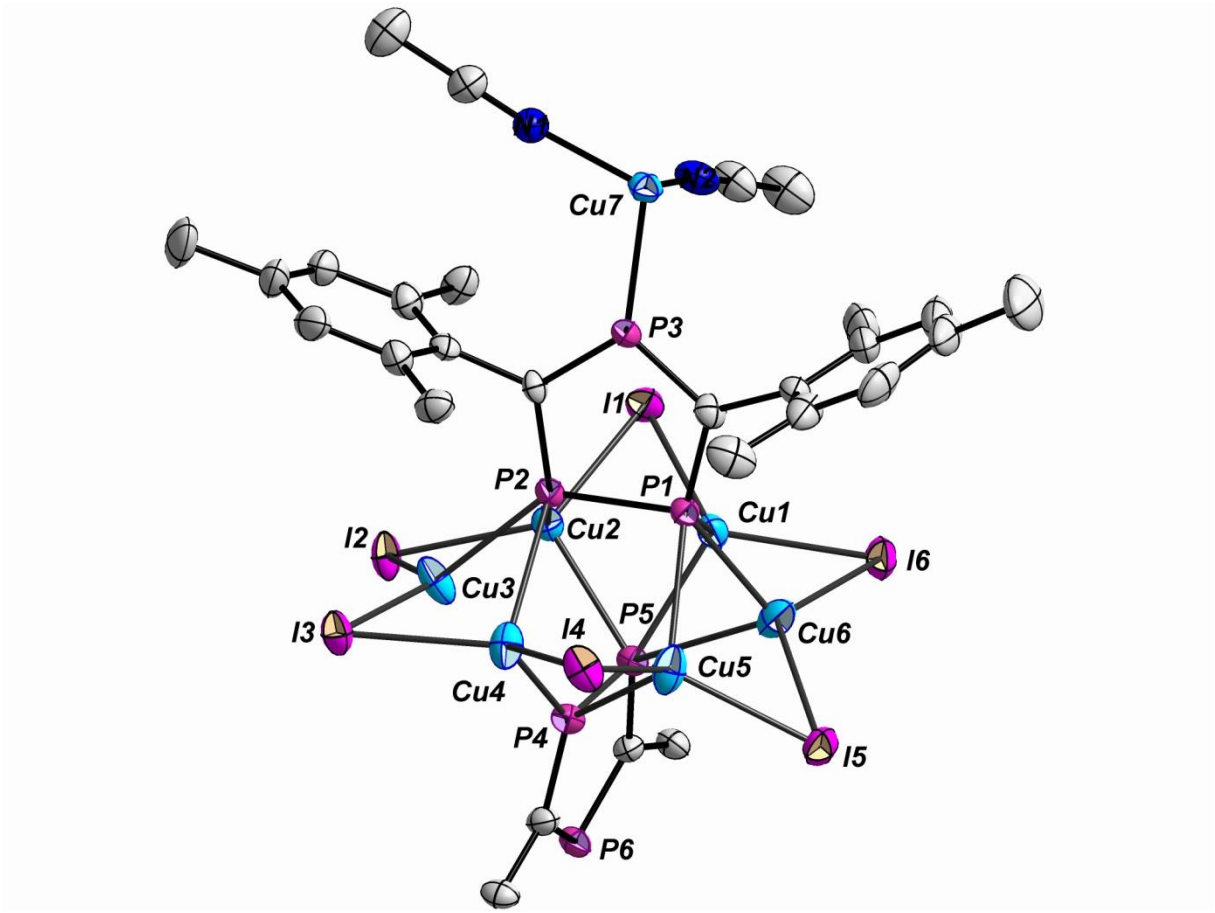


Fig. S 11. Independent part and numbering scheme in **9** · 0.6 CH_2Cl_2. The hydrogen atoms are not shown.

Table S 11. Selected geometric parameters (Å, º) for **9** · 0.6 CH_2Cl_2

Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å	Bond	Distance, Å
I1-Cu1	2.5363 (12)	Cu6-P5	2.835 (2)	Cu1-P1	2.7777 (19)	Fe1-C52	2.054 (9)
I1-Cu2	2.6170 (11)	Cu7-P3	2.2513 (19)	Cu1-P5	2.313 (2)	P1-P2	2.113 (2)
I2-Cu2	2.5947 (11)	Cu7-P6	2.2556 (19)	Cu2-P2	2.458 (2)	P1-C1	1.725 (6)
I2-Cu3	2.5330 (14)	Cu7-N1	1.997 (6)	Cu2-P5	2.4628 (19)	P2-C2	1.717 (6)
I3-Cu3	2.5627 (13)	Cu7-N2	2.019 (6)	Cu3-P2	2.304 (2)	P3-C1	1.742 (6)
I3-Cu4	2.5869 (13)	Fe1-C53	2.072 (9)	Cu3-P4	2.910 (2)	P3-C2	1.736 (6)
I4-Cu4	2.5744 (14)	Fe1-C54	2.066 (9)	Cu4-P2	2.745 (2)	P4-C22^{i}	1.725 (6)
I4-Cu5	2.6066 (13)	Fe1-C55	2.084 (9)	Cu4-P4	2.321 (2)	P4-P5	2.111 (2)
I5-Cu5	2.5919 (13)	Fe1-N3	1.939 (7)	Cu5-P1	2.564 (2)	P5-C21^{i}	1.747 (6)
I5-Cu6	2.5374 (14)	Fe1-N4	1.925 (6)	Cu5-P4	2.498 (2)	P6-C21	1.709 (6)
I6-Cu1	2.5870 (13)	Fe1-N5	1.952 (8)	Cu6-P1	2.315 (2)	P6-C22	1.747 (6)
I6-Cu6	2.6004 (13)	Fe1-C51	2.096 (9)				
Angle	Value, º	Angle	Value, º	Angle	Value, º	Angle	Value, º
N3-Fe1-C52	157.9 (3)	Cu6-P1-P2	126.93 (9)	C52-Fe1-C53	41.3 (4)	Cu5-P4-C22^{i}	132.9 (2)
N3-Fe1-C53	139.4 (4)	Cu2-P2-Cu4	107.05 (7)	C52-Fe1-C54	69.1 (4)	P5-P4-C22^{i}	100.6 (2)
N3-Fe1-C54	101.5 (4)	Cu2-P2-Cu3	64.22 (6)	C52-Fe1-C55	67.6 (4)	Cu4-P4-C22^{i}	129.5 (2)

N3-Fe1-C55	92.0 (3)	Cu3-P2-C2	123.2 (2)	C53-Fe1-C54	40.3 (5)	Cu5-P4-P5	99.12 (8)
N4-Fe1-N5	93.9 (3)	Cu4-P2-P1	91.15 (8)	C53-Fe1-C55	67.4 (4)	Cu4-P4-P5	126.60 (9)
N4-Fe1-C51	153.5 (3)	Cu4-P2-C2	126.8 (2)	C54-Fe1-C55	40.8 (4)	Cu6-P5-C21^{i}	125.8 (2)
N4-Fe1-C52	113.4 (3)	Cu2-P2-P1	100.73 (8)	N3-Fe1-N4	87.9 (3)	P4-P5-C21^{i}	99.9 (2)
N4-Fe1-C53	89.0 (3)	Cu2-P2-C2	120.7 (2)	N3-Fe1-N5	88.3 (3)	Cu2-P5-C21^{i}	124.2 (2)
N4-Fe1-C54	102.9 (3)	Cu3-P2-Cu4	58.32 (6)	N3-Fe1-C51	118.0 (3)	Cu6-P5-P4	89.21 (7)
N4-Fe1-C55	142.7 (3)	Cu3-P2-P1	135.19 (10)	P2-P1-C1	100.1 (2)	Cu1-P5-Cu2	63.46 (5)
N5-Fe1-C51	92.4 (3)	P1-P2-C2	101.1 (2)	Cu1-P1-P2	87.97 (7)	Cu1-P5-Cu6	55.83 (5)
N5-Fe1-C52	95.8 (3)	Cu7-P3-C1	124.6 (2)	Cu1-P1-C1	117.8 (2)	Cu1-P5-P4	130.18 (9)
N5-Fe1-C53	132.3 (4)	Cu7-P3-C2	121.3 (2)	Cu1-P1-Cu5	104.44 (7)	Cu1-P5-C21^{i}	128.7 (2)
N5-Fe1-C54	160.7 (3)	C1-P3-C2	104.2 (3)	Cu1-P1-Cu6	56.74 (5)	Cu2-P5-Cu6	105.77 (7)
N5-Fe1-C55	123.3 (3)	Cu3-P4-C22^{i}	118.0 (2)	Cu5-P1-P2	96.32 (8)	Cu2-P5-P4	100.76 (8)
C51-Fe1-C52	40.3 (4)	Cu4-P4-Cu5	62.36 (6)	Cu5-P1-C1	134.9 (2)	C21-P6-C22	104.4 (3)
C51-Fe1-C53	68.0 (3)	Cu3-P4-P5	87.78 (7)	Cu5-P1-Cu6	62.24 (6)	Cu7-P6-C21	121.4 (2)
C51-Fe1-C54	68.4 (4)	Cu3-P4-Cu4	55.49 (5)	Cu6-P1-C1	130.2 (2)	Cu7-P6-C22	125.3 (2)
C51-Fe1-C55	39.8 (4)	Cu3-P4-Cu5	105.07 (7)				

Symmetry code(s): (i) *x*+1, *y*, *z*.

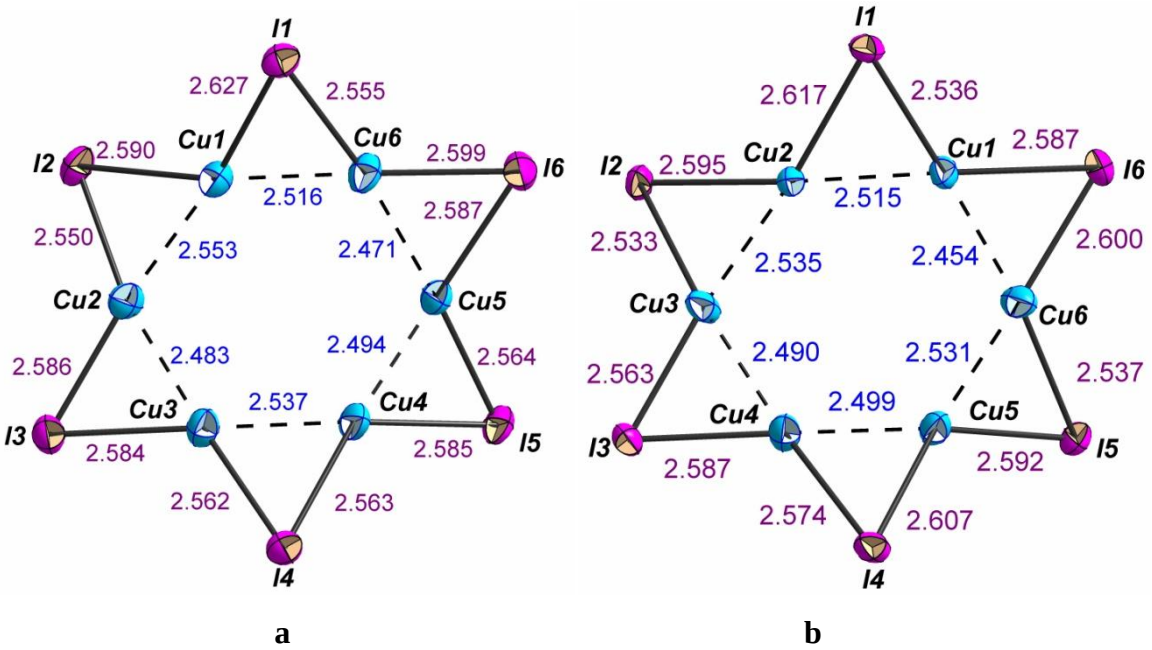


Fig. S 12. Comparison of the geometries of the Cu_6I_6 'hexagram' fragments in (a) **8** · 0.5 CH_2Cl_2 · 3 CH_3CN and (b) **9** · 0.6 CH_2Cl_2.

4. MAS-NMR Details

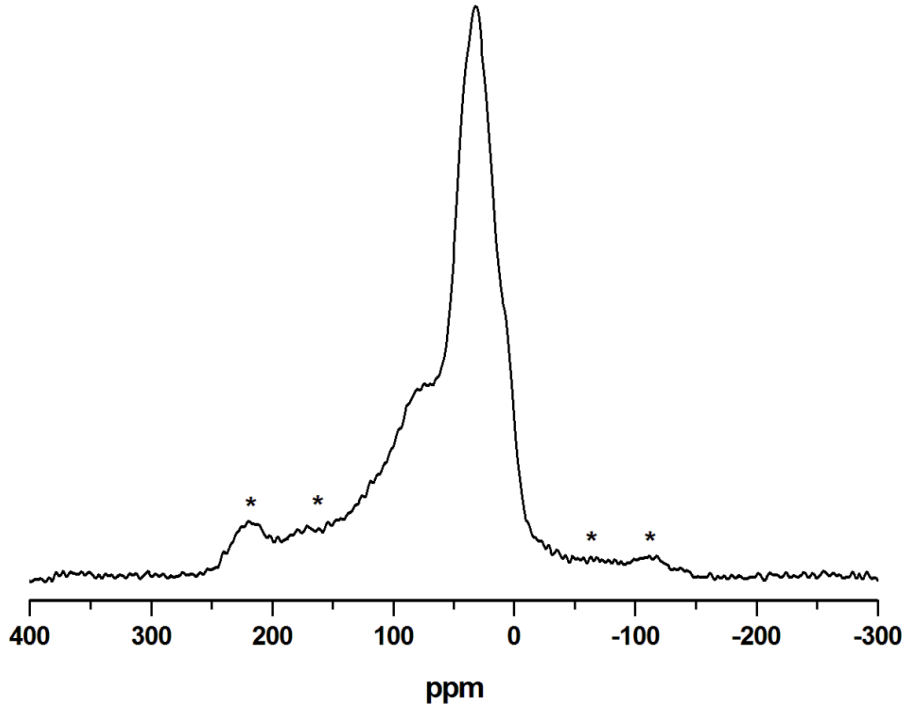


Fig. S13. $^{31}P\{^{1}H\}$ MAS NMR spectrum of **6**, recorded at 202.48 MHz (11.7 T) and 29762 Hz MAS using a commercially available Bruker 2.5 mm HXY triple-resonance probe. The data were obtained using a rotor-synchronized Hahn-Echo (t_R = 33.6µs), 8196 scans were acquired at a relaxation delay of 10s and a rf-field strength of 100 kHz (π/2-pulse of 2.5µs). Spinning sidebands are marked with asterisks.

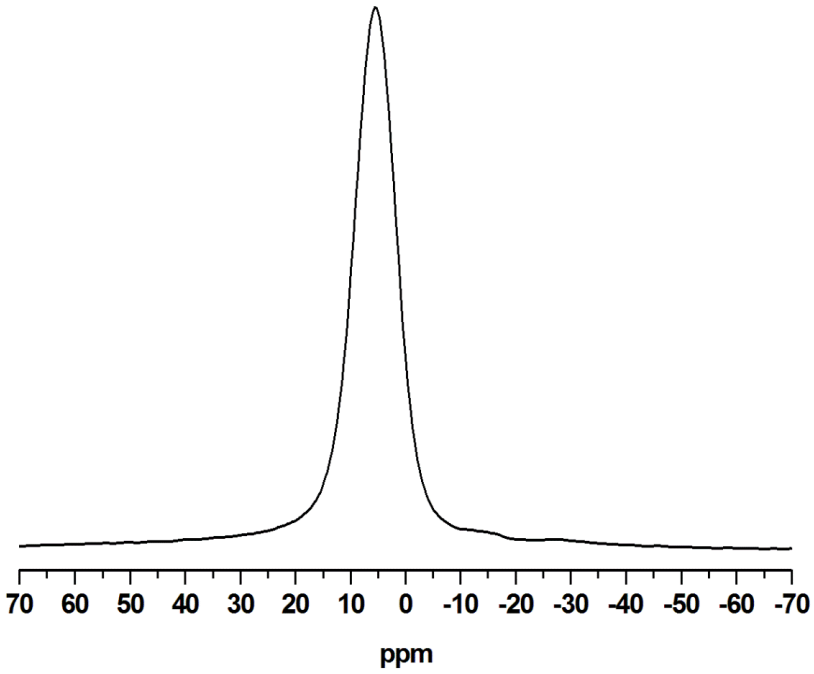


Fig. S14. ^{65}Cu MAS NMR spectrum of **6**, acquired at 142.02 MHz (11.7 T) and 20 kHz MAS using a commercially available Bruker 2.5 mm HXY triple-resonance probe averaging 189.000 Scans at a relaxation delay of 100 ms and a π/12-pulse of 0.5 µs (rf-field strength of 83.3 kHz).

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