Highly soluble Cu(I)-acetonitrile salts as building blocks for novel phosphorus-rich organometallic-inorganic compounds

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General

All manipulations were carried out under an inert atmosphere of dried nitrogen using standard Schlenk techniques. $Cu(CH_3CN)_4BF_4$ and CuCl were purchased from Alfa Aesar and used as received. Li[FAl],[1] Li[TEF],[2] and Tl[TEF][3] were prepared according to literature procedures. Solvents were freshly distilled under argon from Na/K alloy (n-pentane, n-hexane) or from CaH_2 (CH_2Cl_2 and CH_3CN). IR spectra were recorded as KBr discs on varian FTS-800 spectrometer. ^{1}H, ^{13}C, ^{31}P and ^{19}F spectra were recorded on a Bruker Avance 300 or Avance 400 spectrometer. ^{1}H and ^{13}C, ^{31}P and ^{19}F NMR chemical shifts were reported in parts per million (ppm) relative to external standards Me_4Si, H_3PO_4 (85%) or $CFCl_3$. Elemental analysis were performed by the microanalytical laboratory of the Universität Regensburg. Mass spectra were recorded on a ThermoQuest Finnigan TSQ 7000 mass spectrometer.

Synthesis of $[Cu(CH_3CN)_{3.5}][FAl]$ ($[FAl] = [FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$) (1):

1470 mg Li[FAl] (1.05 mmol) and 329 mg $[Cu(CH_3CN)_4][BF_4]$ (1.05 mmol) were placed in a Schlenk vessel equipped with a Young valve and 15 mL of CH_2Cl_2 were added. The vessel was closed under reduced pressure. The reaction was sonicated for one day. This affords a white to grey slurry of very fine powder in a colorless solution. Subsequently the fine white to grey precipitate was removed by centrifugation from the warm CH_2Cl_2 solution. The clear supernatant solution was filtered and the precipitate was washed with 2×15 mL of CH_2Cl_2. The filtrate and washings were combined, concentrated to half volume, layered with *n*-hexane and stored in a fridge to afford clear colorless crystals. The crystals were freed from the mother liquor, washed with *n*-hexane and dried in vacuum. Yield 1278 mg (75%).

^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 2.20$ ppm (s, CH_3). $^{13}C\{^{1}H\}$ NMR (75.47 MHz, CD_2Cl_2): $\delta = 2.79$ ppm (s, CH_3). $^{19}F\{^{1}H\}$ NMR (282.40 MHz, CD_2Cl_2): $\delta = -112.6$ (d, $J_{F,F} = 280$ Hz, 2F), -117.1 (d, $J_{F,F} = 279$ Hz, 2F), -121.5 (d, $J_{F,F} = 277$ Hz, 2F), -127.7 (s, 2F), -130.4 (d, $J_{F,F} = 275$ Hz, 2F), -136.8 (d, $J_{F,F} = 276$ Hz, 2F), -140.7 (d, $J_{F,F} = 277$ Hz, 1F), -154.2 (t, $J_{F,F} = 22$ Hz, 1F), -164.6 (t, JF,F = 18 Hz, 1F), -172.1 ppm (s, AlF). Elemental analysis, calcd. (%) for $[Cu(CH_3CN)_{3.5}][FAl]$: C, 32.51; H, 0.67; N, 3.09. Found: C, 32.26; H, 0.85; N, 3.05. Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 144.8 (100) $[Cu(CH_3CN)_2]^+$, 185.8 (4) $[Cu(CH_3CN)_3]^+$, 226.7 (<1) $[Cu(CH_3CN)_4]^+$; Negative ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 1381.1 (100) $[FAl]^-$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 3216 (vw), 3227 (vw), 3200 (vw), 3021 (vw), 2965 (vw), 2953 (w), 2410 (vw), 2361 (vw), 2323 (w), 2291 (vw), 2274 (vw), 1654 (m), 1536 (s), 1486 (vs), 1407 (w), 1376 (w), 1325 (m), 1310 (m), 1276 (m), 1246 (vs), 1205 (vs).

Synthesis of $[Cu(CH_3CN)_4][TEF]$ ($[TEF] = [Al\{OC(CF_3)_3\}_4]$ (2):

Method 1: 1023 mg Li[TEF] (1.05 mmol) and 329 mg $[Cu(MeCN)_4][BF_4]$ (1.05 mmol) were placed in a Schlenk vessel equipped with a Young valve and 15 mL of CH_2Cl_2 were added. The vessel was closed under reduced pressure. The reaction was sonicated for one day. This affords a white to grey slurry of very fine powder in a colorless solution. Subsequently the fine white to grey precipitate was removed by centrifugation from the warm CH_2Cl_2 solution. The clear supernatant solution was filtered and the precipitate was washed with 2×15 mL of CH_2Cl_2. The filtrate and washings were combined, concentrated to half volume, layered with *n*-hexane at room temperature to afford clear colorless crystals. The crystals were freed from the mother liquor, washed with *n*-hexane and dried in vacuum. Yield 990 mg (79%).

Method 2: 1230 mg Tl[TEF] (1.05 mmol) in 20 ml CH_3CN was added to a stirred solution of CuCl (104 mg, 1.05 mmol) in 20 ml CH_3CN at room temperature. During the addition, a white precipitate of TlCl was formed. After stirring for 10 minutes, the crude mixture was filtered over diatomaceous earth and the solvent removed in vacuum. The white powder was dissolved in a 1:1 mixture of CH_2Cl_2 and CH_3CN and layered with hexane. In few days, **1** can be obtained as colorless blocks. The clear supernatant solution was decanted off, the crystals washed with hexane three times and dried in vacuum. Yield 978 mg (78%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.18 ppm (s, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): δ = 1.91 ppm (s, CH_3), 116.25 (s, CN), 121.2 (q, $^1J_{FC}$ = 293 Hz, CF_3). $^{19}F\{^1H\}$ NMR (376.50 MHz, CD_2Cl_2): δ = -75.6 ppm (s, Al[TEF]). Elemental analysis, calcd. (%) for $[Cu(MeCN)_4][TEF]$: C, 24.12; H, 1.01; N, 4.69. Found: C, 23.74; H, 0.85; N, 4.29. Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 103.96 (40) $[Cu(MeCN)]^+$, 144.98 (100) $[Cu(MeCN)_2]^+$, 186.0 (2) $[Cu(MeCN)_3]^+$; Negative ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 967.0 (100) $[TEF]^-$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2900 (w), 2318 (vw), 2288 (vw), 1355 (w), 1275 (w), 1216 (w), 1158 (w), 1131 (w), 1036 (w), 969 (s), 833 (s), 756 (w), 726 (s), 571 (w), 561 (s), 536 (s), 447 (s).

Synthesis of $[Cu_2\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^1:\eta^1\text{-}P_2)\}_2\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^2\text{-}P_2)\}_2][FAl]_2$ (3):

$[CpMo_2(CO)_4(\eta^2\text{-}P_2)]$ (**A**, 50 mg, 0.10 mmol) and $Cu(CH_3CN)_{3.5}[FAl]$ (**1**, 81 mg, 0.05 mmol) were dissolved in 25 mL of CH_2Cl_2 and stirred for 1 hour at room temperature. The red solution is then filtrated and carefully layered with twofold amount of n-pentane and stored at room temperature. After several days red-orange crystals were formed. The crystals were washed with pentane and dried in vacuum. Yield 88 mg (71%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 5.38 ppm (s, C_5H_5). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 86.4 (s, C_5H_5), 222.9 ppm (s, CO). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ = -84.7 ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_2Cl_2): δ = -112.6 (d, $J_{F,F}$ = 280 Hz, 2F), -117.1 (d, $J_{F,F}$ = 279 Hz, 2F), -121.5 (d, $J_{F,F}$ = 277 Hz, 2F), -127.7 (s, 2F), -130.4 (d, $J_{F,F}$ = 275 Hz, 2F), -136.8 (d, $J_{F,F}$ = 276 Hz, 2F), -140.7 (d, $J_{F,F}$ = 277 Hz, 1F), -154.2 (t, $J_{F,F}$ = 22 Hz, 1F), -164.6 (t, JF,F = 18 Hz, 1F), -172.0 ppm (s, AlF). Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 1051.6 (68) $[Cu\{Cp_2Mo_2(CO)_4P_2\}_2]^+$, Negative ion ESI-MS ($CH_2Cl_2$, RT): *m/z* (%) = 1381.1 (100) $[FAl]^-$, Elemental analysis, calcd. (%) for $[Cu_2(Cp_2Mo_2(CO)_4P_2)_4][FAl]_2$: C, 31.46; H, 1.21; found: C, 30.97; H, 1.24. IR (KBr): $\tilde{\nu}$/cm^{-1}: 3126 (w), 2951 (vw), 2047 (s), 2001 (vs), 1987 (s), 1650 (w), 1538 (m), 1437 (s), 1422 (w).

Synthesis of $[Cu_2\{Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^1:\eta^1\text{-}P_2)\}_2(\eta^1\text{-}CH_3CN)_4][FAl]_2$ (4):

$[CpMo_2(CO)_4(\eta^2\text{-}P_2)]$ (**A**, 50 mg, 0.10 mmol) and $Cu(CH_3CN)_{3.5}[FAl]$ (**1**, 162 mg, 0.10 mmol) were dissolved in 25 mL of CH_2Cl_2 and stirred for 1 hour at room temperature. The red solution is then filtrated and carefully layered with twofold amount of n-pentane and stored at room temperature. After several days red crystals were formed. The crystals were washed with pentane and dried in vacuum. Yield 132 mg (64%).

^1H NMR (300 MHz, CD_2Cl_2): δ = 2.21 (s, CH_3), 5.33 ppm (s, C_5H_5). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ = 2.63 (s, CH_3), 86.0 (s, C_5H_5), 118.80 (s, CN), 222.1 ppm (s, CO). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ = -82.5 ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_2Cl_2): δ = -112.6 (d, $J_{F,F}$ = 280 Hz, 2F), -117.1 (d, $J_{F,F}$ = 279 Hz, 2F), -121.5 (d, $J_{F,F}$ = 277 Hz, 2F), -127.7 (s, 2F), -130.4 (d, $J_{F,F}$ = 275 Hz, 2F), -136.8 (d, $J_{F,F}$ = 276 Hz, 2F), -140.7 (d, $J_{F,F}$ = 277 Hz, 1F), -154.2 (t, $J_{F,F}$ = 22 Hz, 1F), -164.6 (t, *J*F,F = 18 Hz, 1F), -170.2 ppm (s, AlF). Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 1051.0 (42) $[Cu\{Cp_2Mo_2(CO)_4P_2\}_2]^+$, 1098.7 (90) $[Cu(CH_3CN)\{Cp_2Mo_2(CO)_4P_2\}_2]^+$, Negative ion ESI-MS ($CH_2Cl_2$, RT): *m/z* (%) = 1381.0 (100) $[FAl]^-$, Elemental analysis, calcd. (%) for $[Cu_2(Cp_2Mo_2(CO)_4P_2)_2(CH_3CN)_4][FAl]_2$: C, 33.17; H, 0.78; found: C, 33.02; H, 0.94. IR (KBr): $\tilde{\nu}$/cm^{-1}: 3103 (w), 2924 (vw), 2051 (s), 2121 (s), 1994 (s), 1978 (s), 1648 (w), 1530 (m), 1430 (s), 1419 (w).

Synthesis of $[Cu_2\{Cp^*Fe(\mu,\eta^5:\eta^1:\eta^1\text{-}P_5)\}_2(\eta^1\text{-}CH_3CN)_4][FAl]_2$ (5):

$Cp^*Fe(\eta^5\text{-}P_5)$ (**B**, 22 mg, 0.063 mmol) and $Cu(CH_3CN)_{3.5}[FAl]$ (**1**, 100 mg, 0.063 mmol) were weighed together and placed in a Schlenk vessel. To this 25 mL of CH_2Cl_2 were added under constant stirring affording a light brown clear solution. After 24 h stirring, the solution was filtered and layered with the fivefold amount of *n*-hexane and subsequently stored at +4 °C. After several days, compound **5** can be isolated as clear light green crystals which form at the mixing zone of the solvents. The supernatant solution is removed, the crystals are washed with *n*-hexane and dried in vacuum. Yield 89 mg (75%).

^1H NMR (300 MHz, CD_2Cl_2): δ = 1.4 ppm (s, Cp*), 2.10 (s, CH_3CN). $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_2Cl_2): δ = -112.6 (d, $J_{F,F}$ = 280 Hz, 2F), -117.1 (d, $J_{F,F}$ = 279 Hz, 2F), -121.5 (d, $J_{F,F}$ = 277 Hz, 2F), -127.7 (s, 2F), -130.4 (d, $J_{F,F}$ = 275 Hz, 2F), -136.8 (d, $J_{F,F}$ = 276 Hz, 2F), -140.7 (d, $J_{F,F}$ = 277 Hz, 1F), -154.2 (t, $J_{F,F}$ = 22 Hz, 1F), -164.6 (t, $J_{F,F}$ = 18 Hz, 1F), -172.1 ppm (s, AlF). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ = 147.0 ppm (s, P_5). Elemental analysis, calcd. (%) for $[Cu(Cp^*FeP_5)_2(CH_3CN)_4][FAl]$: C, 32.06; H, 1.21; N, 1.37. Found: C, 31.90; H, 1.21; N, 1.37. Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 144.8 (93) $[Cu(MeCN)_2]^+$, 408.7 (100) $[Cu(Cp^*FeP_5)]^+$, 449.8 (95) $[Cu(Cp^*FeP_5)(CH_3CN)]^+$, 754.9 (50) $[Cu(Cp^*FeP_5)_2]^+$; Negative ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 1381.1 (100) $[FAl]^-$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2977 (vw), 2949 (w), 2921 (w), 2851 (vw), 1653 (m), 1534 (s), 1430 (vw), 1407 (vw), 1380 (w), 1324 (m), 1309 (m), 1268 (m), 1244 (s), 1204 (vs).

Synthesis of $[Cu_2\{Cp^*Fe(\mu,\eta^5:\eta^1:\eta^1\text{-}P_5)\}_2(\eta^1\text{-}CH_3CN)_4][TEF]_2$ (6):

$Cp^*Fe(\eta^5\text{-}P_5)$ (**B**, 58 mg, 0.167 mmol) and $Cu(CH_3CN)_4[TEF]$ (**2**, 200 mg, 0.167 mmol) were weighed together and placed in a Schlenk vessel. To this 25 mL of CH_2Cl_2 were added under constant stirring affording a light brown clear solution. After 24 h stirring, the solution was filtered and layered with the twofold amount of *n*-hexane and subsequently stored at room temperature. After several days, compound **6** can be isolated as green blocks. The supernatant solution is removed, the crystals are washed with *n*-hexane three times and dried in vacuum. Yield 131 mg (54%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.90 (s, CH_3CN), 1.38 ppm (s, Cp*). $^{19}F\{^1H\}$ NMR (376.50 MHz, CD_2Cl_2): δ = -78.1 (s, Al[TEF]). $^{31}P\{^1H\}$ NMR (161.97 MHz, CD_2Cl_2): δ = 138.9 ppm (s, P_5). Elemental analysis, calcd. (%) for $[Cu_2(Cp^*FeP_5)_2(CH_3CN)_4][TEF]$: C, 24.70; H, 1.45; N, 1.92. Found: C, 24.68; H, 1.36; N, 1.85. Positive ion ESI-MS (CH_2Cl_2, RT): *m/z* (%) = 449.8 (100) $[Cu(Cp^*FeP_5)(CH_3CN)]^+$, 754.8 (10) $[Cu(Cp^*FeP_5)_2]^+$, 798.7 (2) $[Cu(Cp^*FeP_5)_2(CH_3CN)]^+$; Negative ion ESI-MS ($CH_2Cl_2$, RT): *m/z* (%) = 967.1 (100) $[TEF]^-$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2955(w), 2387 (w), 2314 (w), 2284 (w), 1353 (w), 1379 (w), 1302 (w), 1277 (w), 1216 (w), 1164 (w), 1134 (w), 1074 (w), 973 (s), 832 (w), 755 (w), 727 (s), 5560 (w), 537 (w), 446 (w).

Crystallographic data

The crystals were selected and mounted on a Gemini Ultra diffractometer equipped with an Atlas S2 detector (**1**, **3**, **5**, **6**) and a GV50 diffractometer equipped with a TitanS2 detector (**2**, **4**), respectively. The crystals were kept at T = 123(1) K during data collection. Data collection and reduction were performed with **CrysAlispro** (Version 171.37.34 (**1**), 171.38.43 (**2**, **4**, **6**), 171.39.37b(**3**, **5**)).[4] An Numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK were applied for the compounds (**1**, **4**). For the compounds (**2**, **3**, **5**, **6**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.(Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) using spherical harmonics as implemented in SCALE3 ABSPACK was applied. Using **Olex2**,[5] the structures were solved with **ShelXT**[6] and a least-square refinement on F^2 was carried out with **ShelXL**.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model.

Compound **1**: The asymmetric unit contains two CH_2Cl_2 molecules with occupancies of 1/6 and 1/3 (in total 0.5 CH_2Cl_2 molecules), which are located near a three fold rotation axe and a three fold rotoinversion axe. The F-Al bond of the $[FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$ anion is also located on a three fold rotation axe. Therefore the asymmetric unit contains 1/3 of a $[FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$ anion. The Cu(I) atom is disordered over two close positions (ratio 50:50), which are both located on a three fold rotoinversion axe. One Cu(I) atom is trigonal planar coordinated by three symmetry generated CH_3CN molecules and the other Cu(I) atom is tetrahedral coordinated by four CH_3CN molecules, with one CH_3CN molecule being located on the three fold rotoinversion axe. To describe this disorder the DFIX, SADI, SIMU, RIGU and ISOR restrains as well as the EADP constraint were applied.

Compound **2**: The asymmetric unit contains a free CH_3CN solvent molecule and 4 CH_3CN molecules coordinated to a Cu(I) atom. Further it contains a $[Al\{OC(CF_3)_3\}_4]$ anion. Three of the $\{OC(CF_3)_3\}$ groups of the anion are disordered. To describe this disorder the SADI, SIMU and ISOR restrains were applied.

Compound **3**: The asymmetric unit contains 2 CH_2Cl_2 solvent molecules, which were heavily disordered. Therefore, a solvent mask was calculated and 184.0 electrons were found in a volume of 697.0\% Å^3 in 3 voids. This is consistent with the presence of 2 CH_2Cl_2 molecules per formula unit, which account for 168.0 electrons. The asymmetric unit further contains a Cu(I) atom, a $[FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$ anion and two $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$ complexes. One of these complexes shows a disorder of a Cp and CO ligand over two positions (51:49). To describe this disorder the SIMU restrain was applied.

Compound **4**: The asymmetric unit contains 0.5 CH_2Cl_2 solvent molecules and two CH_3CN molecules coordinated to a Cu(I) atom. Further it contains a $[FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$ anion and a $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$ complex. The Cp and CO ligands of this complex are each disordered over two positions with a ratio of 92:8 and 83:17, respectively. To describe this disorder the DFIX, SADI, SIMU and RIGU restrains were applied.

Compound **5**: The asymmetric unit contains 1 CH_2Cl_2 solvent molecule, which was heavily disordered. Therefore, a solvent mask was calculated and 168.0 electrons were found in a volume of 660.0\% Å^3 in 2 voids. This is consistent with the presence of a CH_2Cl_2 molecule per formula unit, which account for 168.0 electrons. The asymmetric unit further contains a Cu(I) atom, which is coordinated by two CH_3CN molecules, a $[FAl\{OC(C_6F_{10})(C_6F_5)\}_3]$ anion and a $[Cp^*Fe(\eta^5\text{-}P_5)]$ complexes. The two acetonitriles are disordered over two positions with a ratio of 56 to 44. To describe this disorder the SADI and SIMU restrains were applied.

Compound **6**: The asymmetric unit contains a CH_2Cl_2 solvent molecule, which is disordered over three positions with occupancies refined as 0.52, 0.28 and 0.20. The asymmetric unit further contains a Cu(I) atom, which is coordinated by two CH_3CN molecules, a $[Al\{OC(CF_3)_3\}_4]$ anion and a $[Cp^*Fe(\eta^5\text{-}P_5)]$ complex. All four $\{OC(CF_3)_3\}$ groups of the anion are disordered. Three $\{OC(CF_3)_3\}$ groups are disordered over two positions and one $\{OC(CF_3)_3\}$ group is disordered over three positions. To describe this disorder the SADI, SIMU and ISOR restrains were applied.

CCDC-1866456 (**1**), CCDC-1866457 (**2**), CCDC-1866458 (**3**), CCDC-1866459 (**4**), CCDC-1866460 (**5**)and CCDC-1866461 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Compound	**1**	**2**	**3**
Experiment Name	MF439_new	oP_abs_det_ana	abs249_ap_abs
CCDC	1866456	1866457	1866458
Formula	$C_{88.98}H_{26.96}Al_2Cl_{5.96}Cu_2F_{92}N_7O_6$	$C_{26}H_{15}AlCuF_{36}N_5O_4$	$AlC_{66}Cl_4CuF_{46}H_{24}Mo_4O_{11}P_4$
$D_{calc.}$/ g cm^{-3}	2.028	1.900	2.051
μ/mm^{-1}	3.895	2.782	1.197
Formula Weight	3430.22	1235.95	2606.81
Colour	clear colourless	clear light colourless	red
Shape	block	block	block
Size/mm^3	0.27×0.21×0.18	0.26×0.21×0.13	0.26×0.20×0.10
T/K	123.1(3)	122.95(18)	123.0(10)
Crystal System	trigonal	orthorhombic	triclinic
Flack Parameter	-	-0.009(17)	-
Hooft Parameter	-	0.007(13)	-
Space Group	P-3	$P2_12_12_1$	P-1
a/Å	14.36351(9)	10.61200(10)	11.2007(3)
b/Å	14.36351(9)	17.1552(2)	18.7374(4)
c/Å	15.72381(12)	23.7300(3)	21.9873(6)
α/°	90	90	111.280(2)
β/°	90	90	95.785(2)
γ/°	120	90	96.565(2)
V/Å^3	2809.37(4)	4320.07(8)	4220.9(2)
Z	1	4	2
Z'	0.16667	1	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	CuK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$
Θ_{min}/°	3.553	3.179	3.500
Θ_{max}/°	65.981	75.333	32.603
Measured Refl.	54098	13779	41468
Independent Refl.	3271	8404	26612
Reflections with I > 2(I)	3049	7937	18298
R_{int}	0.0329	0.0223	0.0396
Parameters	375	990	1244
Restraints	66	99	42
Largest Peak	0.287	0.262	1.530
Deepest Hole	-0.689	-0.361	-2.018
GooF	1.049	1.046	0.959
wR_2 (all data)	0.0732	0.0810	0.1126
wR_2	0.0721	0.0790	0.0994
R_1 (all data)	0.0313	0.0334	0.0770
R_1	0.0293	0.0311	0.0479
Diffractometer	Gemini Ultra	GV50	Gemini Ultra
Absorption correction	gaussian	analytical	analytical

Compound	**4**	**5**	**6**
Experiment Name	abs282_abs	mf450_mp_abs	mp_abs_ana
CCDC	1866459	1866460	1866461
Formula	$C_{109}H_{34}Al_2Cl_2Cu_2F_{92}Mo_4N_4O_{14}P_4$	$C_{51}H_{23}AlCl_2CuF_{46}FeN_2O_3P_5$	$C_{31}H_{23}AlCl_2CuF_{36}FeN_2O_4P_5$
$D_{calc.}$/ g cm^{-3}	2.036	1.926	1.925
μ/mm^{-1}	6.005	5.706	1.104
Formula Weight	4130.98	1957.83	1543.63
Colour	clear light orange	clear light green	clear light green
Shape	block	block	block
Size/mm^3	0.32×0.27×0.18	0.33×0.26×0.11	0.30×0.28×0.23
T/K	122.9(2)	123.1(2)	123(1)
Crystal System	monoclinic	monoclinic	monoclinic
Flack Parameter	-	-	-
Hooft Parameter	-	-	-
Space Group	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	28.2675(2)	11.46563(4)	10.9037(3)
b/Å	18.77190(10)	19.19874(6)	27.5664(6)
c/Å	25.8322(2)	30.69781(11)	17.8993(3)
α/°	90	90	90
β/°	100.4620(10)	92.1269(3)	98.166(2)
γ/°	90	90	90
V/Å^3	13479.58(16)	6752.72(4)	5325.5(2)
Z	4	4	4
Z'	0.5	1	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	CuK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$
Θ_{min}/°	3.479	3.688	3.227
Θ_{max}/°	67.079	66.092	32.321
Measured Refl.	35932	109308	55908
Independent Refl.	11993	11781	16663
Reflections with I > 2(I)	11733	11618	13655
R_{int}	0.0267	0.0258	0.0241
Parameters	1198	1047	1514
Restraints	230	144	2709
Largest Peak	1.187	0.309	0.665
Deepest Hole	-0.796	-0.467	-0.496
GooF	1.031	1.035	1.023
wR_2 (all data)	0.0974	0.0674	0.1003
wR_2	0.0968	0.0671	0.0932
R_1 (all data)	0.0370	0.0272	0.0522
R_1	0.0364	0.0269	0.0398
Diffractometer	GV50	Gemini Ultra	Gemini Ultra
Absorption correction	gaussian	analytical	analytical

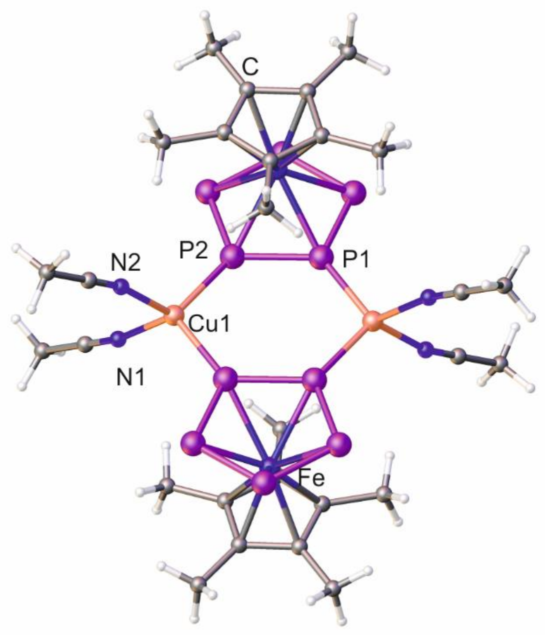

Figure S1: Representation of the solid state structure of compound **6**. The anions and solvent molecules are omitted for clarity.

References

[1] T. Köchner, N. Trapp, T. A. Engesser, A. J. Lehner, C. Röhr, S. Riedel, C. Knapp, H. Scherer, I. Krossing, *Angew. Chem. Int. Ed.* **2011**, *50*, 11253-11256; *Angew. Chem.* **2011**, *123*, 11449-11452.

[2] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490-502.

[3] M. Gonsior, I. Krossing, N. Mitzel, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1821-1830.

[4] CrysAlisPro Software System, Rigaku Oxford Diffraction (2015).

[5] O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **2009**, 42, 339-341.

[6] G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.* **2015**, A71, 3-8.

[7] G. M. Sheldrick, Crystal structure refinement with ShelXL, *Acta Cryst.* **2015**, C27, 3