Organometallic polyphosphorus and -arsenic ligands as linkers between pre-assembled linear Cu^{I} fragments

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Experimental section

General considerations

All manipulations were carried out under an inert atmosphere of dried nitrogen using standard Schlenk and drybox techniques. THF was dried with Na. MeCN, CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2. NMR spectra were recorded in CD_2Cl_2 on a Bruker Avance 300 MHz NMR spectrometer (^{1}H: 300.132 MHz, ^{31}P: 121.495 MHz, ^{13}C: 75.468 MHz, ^{19}F: 282.404 MHz) or a Bruker Avance 400 MHz NMR spectrometer (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz, ^{13}C: 100.613 MHz, ^{11}B: 128.378 MHz). IR spectra were recorded as KBr discs using a Varian FTS-800 FT-IR spectrometer. Electron spray ionization mass spectra were recorded by the MS department of the University of Regensburg on a ThermoQuest Finnigan TSQ 7000 mass spectrometer. Elemental analyses were performed by the micro analytical laboratory of the University of Regensburg.

Synthesis of the compounds 1-6:

Preparation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+[BF_4]^-$ (**1**): 101 mg (2eq., 0.2 mmol) dpmp, 32 mg (1eq., 0.1 mmol) $[Cu(MeCN)_4][BF_4]$ and 20 mg (2eq., 0.2 mmol) CuCl were weighed into a Schlenk flask and 10 mL CH_2Cl_2 were added under constant stirring. The cloudy solution turns clear in the course of five minutes. After 24 hours of stirring at room temperature, this solution can either be used for further reaction with the desired P_n or As_n ligands or filtrated and layered with *n*-pentane. This affords colorless crystals in 73 % yield (99 mg). ^{1}H NMR (400 MHz, CD_2Cl_2) d 7.70 - 6.58 (m, 50H, Ph), 3.81 - 3.00 (multiple overlapping signals, CH_2); ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2) d –6.54 (m, small signal), –11.17 (m, small signal), –14.30 (m, $RPPh_2$), –17.27 (br, R_2PPh); ^{11}B{^{1}H} NMR (128.4 MHz, CD_2Cl_2) d –0.95 ($^0BF_4$); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2) 133.65 - 127.49 (multiple signals, Ph), 28.16 (CH_2). IR(KBr) cm^{-1}:3072 (vw), 3052 (w), 3020 (vw), 2955 (vw), 2924 (vw), 2896 (vw), 2854 (vw), 1587 (vw), 1574 (vw), 1485 (m), 1436 (s), 1377 (m), 1333 (vw), 1310 (vw), 1278 (vw), 1189 (vw), 1159 (vw), 1099 (s), 1084 (m), 1065 (m), 1028 (m) 999 (m), 794 (m), 739 (s), 691 (s).

General preparation procedure of the compounds **2-5**: A solution of **1** was prepared as described above. After 24 hours of stirring the P_n or As_n ligand complex (0.1 mmol, 1eq.) was dissolved in a small amount of CH_2Cl_2 and added dropwise to this solution. This reaction was degassed five times and stirred for another 24 hours. Afterwards the solution was filtered and *n*-pentane diffusion into the solution afforded the crystalline products in a course of several days.

Isolation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}P_2)Mo_2(CO)_2Cp_2\}][BF_4]$ (**2**): 50 mg **A1** (1 eq., 0.1 mmol) added in a small amount of CH_2Cl_2 to a 1:1 stoichiometric solution of **1**. After 24 hours stirring, subsequent filtration and layering with *n*-pentane, compound **2** was isolated as orange to red plates in 51 % yield (95 mg, 0.051 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2) d 7.70 - 6.55 (m, 50H, Ph), 5.11 (s, 9H, Cp), 3.63 (m, 3.5H, CH_2), 3.38 (m, 1H, CH_2), 3.10 (m, 3.5H, CH_2); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) d –6.68 (br m, small signal), –11.35 (br m, small signal), –15.28 (m, $RPPh_2$), –19.72 (br, R_2PPh), –65.60 (s, P_2); ^{19}F NMR (282.4 MHz, CD_2Cl_2) d –148.75 ($^{10}BF_4$), –148.81 ($^{11}BF_4$); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) 226.53 (CO), 134.61 - 128.15 (multiple signals, Ph), 87.52 (Cp), 30.48 (CH_2). Positive ion MS, q/m (%): 1273.2 (100) $[Cu_3Cl_2(dpmp)_2]^+$. Negative ion MS, q/m (%): 1447.3 (100) $[Cu_3Cl_2(dpmp)_2(BF_4)_2]^-$. IR(KBr) cm^{-1}: 3117 (vw), 3079 (vw), 3052 (w), 3005 (w), 2987 (w), 2954 (vw), 2917 (vw), 2851 (vw), 2000 (m), 1991 (m), 1965 (vs), 1925 (s), 1908 (s), 1848 (m), 1629 (w), 1485 (m), 1435 (s), 1377 (w), 1098 (s), 1084 (s). Anal. calcd for $Cu_3Cl_2(dpmp)_2\{Cp_2Mo_2(CO)_4P_2\}(BF_4)(CH_2Cl_2)_{0.3}$: C, 49.95; H, 3.67. Found: C, 49.98; H, 3.62.

Isolation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}As_2)Mo_2(CO)_2Cp_2\}][BF_4]$ (**3**): 59 mg **A2** (1 eq., 0.1 mmol) added in a small amount of CH_2Cl_2 to a 1:1 stoichiometric solution of **1**. After 24 hours stirring, subsequent filtration and layering with *n*-pentane, compound **3** was isolated as dark red blocks in 43 % yield (84 mg, 0.043 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2) d 7.72 - 6.54 (m, 50H, Ph), 5.11 (s, 8H, Cp), 3.81 - 3.00 (multiple overlapping signals, CH_2); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) d –7.12 (br m, small signal), –11.35 (br m, small signal), –14.53 (m, $RPPh_2$), –17.42 (br, R_2PPh); ^{19}F NMR (282.4 MHz, CD_2Cl_2) d –149.67 ($^{10}BF_4$), –149.73 ($^{11}BF_4$); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2), 131.05 - 126.25 (multiple signals, Ph), 84.99 (Cp). Positive ion MS, q/m (%): 1273.0 (100) $[Cu_3Cl_2(dpmp)_2]^+$, 1879.4 (0.55) $[Cu_4Cl_3(dpmp)_3]^+$, 1979.2 (0.25) $[Cu_5Cl_4(dpmp)_3]^+$. IR(KBr) cm^{-1}: 3081 (vw), 3053 (w), 2955 (vw), 2919 (vw) 2898 (vw), 2851 (vw), 1978 (w), 1954 (vs), 1913 (s), 1896 (s), 1630 (w), 1485 (w), 1435 (m), 1378 (w), 1098 (m), 1084 (m). Anal. calcd for $Cu_3Cl_2(dpmp)_2\{Cp_2Mo_2(CO)_4As_2\}(BF_4)(CH_2Cl_2)$: C, 46.74; H, 3.48. Found: C, 46.88; H, 3.65.

Isolation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^1{:}\eta^5\text{-}P_5)FeCp^*\}]_n[BF_4]_n$ (**4**): 35 mg **A1** (1 eq., 0.1 mmol) added in a small amount of CH_2Cl_2 to a 1:1 stoichiometric solution of **1**. After 24 hours stirring, subsequent filtration and layering with *n*-pentane, compound **4** was isolated as green rods in 47 % yield (81 mg, 0.047 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2) d 7.72 - 6.55 (m, 50H, Ph), 3.81 - 3.01 (multiple overlapping signals, CH_2), 1.42 (s, 14H, Cp*); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) d 149.91 (s, P_5), –6.92 (br m, small signal), –11.33 (br m, small signal), –14.62 (m, $RPPh_2$), –18.35 (br, R_2PPh); ^{19}F NMR (282.4 MHz, CD_2Cl_2) d –149.35 ($^{10}BF_4$), –149.40 ($^{11}BF_4$); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) 134.84 - 128.31 (multiple signals, Ph), 91.82 (Cp*) 30.23 (CH_2), 11.06 (CH_3). Positive ion MS, q/m (%): 1272.9 (100) $[Cu_3Cl_2(dpmp)_2]^+$, 1782.3 (3.0) $[Cu_3Cl_2(dpmp)_3]^+$. Negative ion MS, q/m (%): 87.1 (100) $[BF_4]^-$. IR(KBr) cm^{-1}:3072 (vw), 3051 (w), 3017 (vw), 2954 (vw), 2908 (vw) 1436 (m), 1376 (w), 1124 (w), 1097 (w), 1084 (m), 1026 (w) 1000 (w), 791 (w), 738 (m), 690 (m), 669 (m). Anal. calcd for $Cu_3Cl_2(dpmp)_2\{Cp^*FeP_5\}(BF_4)(CH_2Cl_2)_{1.3}$: C, 49.76; H, 4.19. Found: C, 49.73; H, 4.26.

Isolation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^1{:}\eta^5\text{-}As_5)FeCp^*\}]_n[BF_4]_n$ (**5**): 57 mg **B2** (1 eq., 0.1 mmol) added in a small amount of CH_2Cl_2 to a 1:1 stoichiometric solution of **1** which resulted in an immediate color change from olive green color of complex **B2** to dark red. After 24 hours stirring, subsequent filtration and layering with *n*-pentane, compound **5** was isolated as brown blocks in 36 % yield (70 mg, 0.036 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2) d 7.70 - 6.55 (m, 50H, Ph), 3.81 - 3.03 (multiple overlapping signals, CH_2), 1.37 (s, 13H, Cp*); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) d –6.82 (br m, small signal), –11.34 (br m, small signal), –14.44 (m, $RPPh_2$), –17.25 (br, R_2PPh); ^{19}F NMR (282.4 MHz, CD_2Cl_2) d –149.36 ($^{10}BF_4$), –149.41 ($^{11}BF_4$); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) 134.71 - 128.06 (multiple signals, Ph), 88.01 (Cp*) 30.32 (CH_2), 12.27 (CH_3). Positive ion MS, q/m (%): 2583.6, (20) $[Cu_6Cl_5(dpmp)_4]^+$; 1977.8, (10) $[Cu_5Cl_4(dpmp)_3]^+$; 1879.6, (5) $[Cu_4Cl_3(dpmp)_3]^+$; 1273.0, (100) $[Cu_3Cl_2(dpmp)_2]^+$; 665.1, (5) $[Cu_2Cl(dpmp)]^+$; 619.2, (17) $[Cu_3Cl(dpmp)_2]^{2+}$; 569.1, (3) $[Cu(dpmp)]^+$. Negative ion MS, q/m (%): 87.2, (100) $[BF_4]^-$. IR(KBr) cm^{-1}: 3072 (w), 3051 (m), 3019 (vw), 3005 (vw), 2986 (vw), 2952 (w), 2899 (w), 2360 (vw), 2342 (vw), 1625 (w), 1587 (w), 1574 (w), 1484 (m), 1435 (vs), 1375 (m), 1124 (m), 1098 (s), 1084 (vs), 1064 (s), 1026 (m), 999 (m). Anal. calcd for $Cu_3Cl_2(dpmp)_2\{Cp^*FeAs_5\}(BF_4)(CH_2Cl_2)$: C, 44.77; H, 3.76. Found: C, 44.80; H, 4.01.

Preparation of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[BF_4]^-$ (**6**): The literature reports of one structurally characterized related trinuclear Cu^I complex ($[Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[ClO_4]^-\bullet H_2O$).[i] We were able to synthesize the same cationic complex with $[BF_4]^-$ as an anion. Therefore we followed a one-pot synthesis to obtain compound **1** with two terminal MeCN ligands.

101 mg (2eq., 0.2 mmol) dpmp, 32 mg (1eq., 0.1 mmol) $[Cu(MeCN)_4][BF_4]$ and 20 mg (2eq., 0.2 mmol) CuCl were weighed into a Schlenk flask and a solvent mixture of 8 mL THF and 2 mL MeCN were added under constant stirring. The compounds dissolved to form a clear and colorless solution in about 30 to 60 seconds. After 24 hours of stirring at room temperature the solution was filtered vapor diffusion of Et_2O into the solution affords colorless crystal in the course of some days. The mother liquor is decanted off the crystals. The crystals are washed with Et_2O a few times and dried in vacuum for 30 minutes. After this time about 0.6 equivalents of the coordinated MeCN ligands could be removed from the crystals as indicated by elemental analysis. By grinding the sample and drying it in vacuum for another 2 hours, the MeCN could completely be removed. Yield 66% (95 mg)

Sample dried for 30 minutes:
Anal. calcd for $Cu_3Cl_2(dpmp)_2(MeCN)_{1.4}(BF_4)$: C, 56.55; H, 4.42; N, 1.38. Found: C, 56.55; H, 4.70; N, 1.35.
Sample grinded and dried for 2 hours:
Anal. calcd for $Cu_3Cl_2(dpmp)_2(BF_4)$: C, 56.47; H, 4.29; N, 0.00. Found: C, 56.27; H, 4.35; N, 0.00.
Positive ion MS, q/m (%): 1273.4 (100) $[Cu_3Cl_2(dpmp)_2]^+$, 1175.3 (7) $[Cu_2Cl_1(dpmp)_2]^+$, 669.0 (10) $[Cu_2Cl(dpmp)]^+$, 569.1 (8) $[Cu(dpmp)]^+$. Negative ion MS, q/m (%): 87.1 (100) $[BF_4]^-$. IR(KBr) cm^{-1}: 3052 (w), 2956 (vw), 2895 (vw), 1587 (vw), 1574 (vw), 1485 (m), 1436 (s), 1377 (m), 1333 (vw), 1309 (vw), 1278 (vw), 1189 (vw), 1159 (vw), 1099 (s), 1084 (s), 1028 (m) 1000 (m), 793 (m), 738 (s), 691 (s).

Dynamic coordination behavior of the parent [Cu_3] building block (1)

The parent compound $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+[BF_4]^-$ (**1**) is prepared in a straightforward manner by dissolving two equivalents dpmp and CuCl together with one equivalent of $[Cu(MeCN)_4][BF_4]$. The use of MeCN/THF (1:5) mixtures as solvent afforded the desired building block **1** with terminal MeCN ligands $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[BF_4]^-$ (**6**) (see Figure 1 for a representation of the solid state structure). A related compound $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[ClO_4]^-\bullet H_2O$ was described in the literature before, following a different synthetic approach.[i] When the substitution of the labile MeCN ligands by our P_n or As_n ligand complexes was tried in MeCN/THF mixtures we could never observe any coordination to the Cu ions.

Therefore, we prepared the parent compound **1** in pure CH_2Cl_2 without THF or MeCN addition. After stirring CuCl, dpmp and $[Cu(MeCN)_4][BF_4]$ in CH_2Cl_2 and subsequent vapor diffusion of *n*-pentane into the solution, we were able to isolate the parent cationic building block $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+[BF_4]^-$ (**1**) without MeCN ligands. This was an astonishing result, since the central cationic cluster $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$ is still intact, but is now also exhibiting two vacant coordination sites on the outer Cu ions. Consequently, we performed our following coordination chemistry only in CH_2Cl_2 solution.

When crystals of the pure $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$ building block (=$[Cu_3]$) are dissolved in CD_2Cl_2 at –80 °C the $[Cu_3]$ cluster remains intact and two broad signals can be identified in the $^{31}P\{^1H\}$ NMR spectrum at –15.3 ppm and at –17.4 ppm in a 2:1 ratio for the dpmp ligand. The ^1H NMR spectrum at –80 °C shows next to the aromatic protons of the phenyl rings two broad signals at 3.06 ppm and at 3.58 ppm for the diastereotopic atoms of the methylene groups of the bridging dpmp ligands. When the solution is warmed up in the NMR spectrometer the $[Cu_3]$ cluster seems to show some dynamic behavior above –20 °C which can be monitored by new signals arising next to the ones of the $[Cu_3]$ cluster which is still the major part in solution even at room temperature. When the same solution is cooled down again, the ^1H and the $^{31}P\{^1H\}$ NMR spectra do not change and do not show the initial

signals for the pure [Cu_3] cluster. Thus, we assume a dynamic coordination behavior that needs some thermal energy for breaking the dative Cu–P bonds and cooling down the solution of the dissociated compounds will not reverse the process to form the desired coordination complexes. This formation can be realized during the crystallization process by the addition of the investigated P_n and As_n ligand complexes to the [Cu_3] building block in CH_2Cl_2 and subsequent vapor diffusion of *n*-pentane into the solution. This affords the desired coordination complexes formed from the [Cu_3] cluster coordinated by the P or As atoms of the E_n ligands. The ^{1}H NMR spectra of the isolated products in CD_2Cl_2 at room temperature show the same set of signals as the pure [Cu_3] building block and an additional singlet for the Cp rings of [$Cp_2Mo_2(CO)_4(\mu,\eta^2{:}\eta^2\text{-}E_2)$] (E = P(**A1**), As(**A2**)) or the Cp* ring of [$Cp^*Fe(\eta^5\text{-}E_5)$] (E = P(**B1**), As(**B2**)). The $^{31}P\{^1H\}$ NMR spectrum of complex **2** additionally shows a singlet at –65.6 ppm for the P_2 ligand **A1** which is shifted 21 ppm upfield compared to the free complex **1**. The $^{31}P\{^1H\}$ NMR spectrum of the one-dimensional coordination polymer **4** also shows a singlet at 149.9 ppm for the P_5 ring of complex **B1** which is shifted 3 ppm upfield compared to the free ligand **B1**. The observed singlets for the P_n ligands in the $^{31}P\{^1H\}$ NMR spectra of the products **2** and **4** show that the P atoms are equivalent on the NMR timescale and show a dynamic behavior.

All isolated compounds (**1-6**) always exhibit the cationic building block $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$ and we never saw any other combination of Cu^+ and the dpmp ligand in the solid state. The ^{1}H NMR as well as the ^{31}P NMR spectra of isolated crystals of the compounds **1-5** dissolved in CD_2Cl_2 at room temperature show a dynamic coordination behavior and suggest that the well-defined arrangement of the described coordination units in the solid state structures are formed during the crystallization process. From these observations we can conclude, that the $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$ building block is a very stable aggregate, since it is exclusively observed in the solid state, but in solution different Cu^+ species with dpmp and Cl^- ligands are in equilibrium.

X-ray Crystallography

All crystal preparations were done under mineral oil. The data collection was either performed on an Agilent Technologies SuperNova diffractometer equipped with a micro focus Cu X-ray source, an Agilent Technologies Gemini R Ultra equipped with sealed tube Mo and Cu X-ray sources or on a Bruker Apex II difractometer equipped with a Mo X-ray source. All measurements were performed at 150 K or at 123 K by nitrogen cooling. The structure least square refinement was done with the SHELX program package[ii] against F^2.

Table 1. Crystallographic details for the compounds 1-3.

	1	**2**	**3**
Empirical formula	$C_{66}H_{62}BCl_6Cu_3F_4P_6$	$C_{80}H_{72}BCl_6Cu_3F_4Mo_2O_4P_8$	$C_{80}H_{72}As_2BCl_6Cu_3F_4Mo_2O_4P_6$
M [gmol^{-1}]	1531.14	2027.18	2115.08
Crystal size [mm]	0.18 × 0.13 × 0.04	0.17 × 0.10 × 0.02	0.27 × 0.14 × 0.03
T [K]	123(1)	123(1)	123(1)
λ [Å]	1.54178	1.54178	1.54178
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	12.4596(1)	12.8855(1)	12.8880(2)
b [Å]	27.6079(2)	43.5442(4)	43.5784(5)
c [Å]	20.0624(2)	14.9499(1)	15.0001(2)
α [°]	90	90	90
β [°]	104.466(1)	95.216(1)	95.152(2)
γ [°]	90	90	90
V [Å^3]	6682.34(10)	8353.49(12)	8390.6(2)
Z	4	4	4
ρ_{calc} [gcm^{-3}]	1.522	1.612	1.674
μ [mm^{-1}]	5.096	6.923	7.403
diffractometer	Agilent SuperNova	Agilent SuperNova	Agilent SuperNova
radiation	Cu–K_α	Cu–K_α	Cu–K_α
θ range [°]	3.20 – 70.07	3.14 – 73.67	3.13 – 66.59
absorption correct.	analytical	analytical	analytical
T_{min} / T_{max}	0.548 / 0.832	0.515 / 0.887	0.262 / 0.791
reflns collect / unique	38396 / 12632	60821 / 16362	62003 / 14787
reflns obs [$I>2\sigma(I)$]	10855	15012	12776
R_{int}	0.0236	0.0462	0.0513
parameters / restraints	781 / 0	1055 / 110	1078 / 103
GOF on F^2	1.123	1.065	1.037
R_1 / wR_2 [$I>2\ \sigma(I)$]	0.0299 / 0.0869	0.0506 / 0.1293	0.0465 / 0.1178
R_1 / wR_2 (all data)	0.0369 / 0.0950	0.0548 / 0.1315	0.0534 / 0.1214
max / min $\Delta\rho$[eÅ^{-3}]	0.866 / –0.764	1.732 / –1.124	0.784 / –1.024

Table 2. Crystallographic details for the compounds 4-6.

	4	**5**	**6**
Empirical formula	$C_{74}H_{73}BCl_2Cu_3F_4FeP_{11}$	$C_{76}H_{77}As_5BCl_6Cu_3F_4FeP_6$	$C_{68}H_{64}BCl_2Cu_3F_4N_2P_6$
M [gmol^{-1}]	1707.21	2096.81	1443.39
Crystal size [mm]	0.43 × 0.17 × 0.11	0.13 × 0.11 × 0.06	0.60 × 0.45 × 0.33
T [K]	123(1)	123(1)	150(1)
λ [Å]	0.71073	1.54178	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	12.5098(3)	12.5858(1)	12.7414(4)
b [Å]	25.2944(6)	24.4849(2)	13.4211(4)
c [Å]	27.8308(5)	27.9362(2)	21.4040(7)
α [°]	90	90	85.562(3)
β [°]	97.692(2)	98.748(1)	72.949(3)
γ [°]	90	90	79.079(3)
V [Å^3]	8727.2(3)	8508.73(12)	3435.0(2)
Z	4	4	2
ρ_{calc} [gcm^{-3}]	1.299	1.637	1.395
μ [mm^{-1}]	1.443	7.545	1.190
diffractometer	Agilent Gemini R Ultra	Agilent Gemini R Ultra	Bruker Apex II
radiation	Mo–K_α	Cu–K_α	Mo–K_α
θ range [°]	3.04 – 27.10	3.20 – 66.64	2.49 – 27.38
absorption correct.	analytical	analytical	multi-scan
T_{min} / T_{max}	0.705 / 0.878	0.541 / 0.792	0.6342 / 0.7456
reflns collect / unique	64795 / 19018	61670 / 14620	24359 / 15299
reflns obs [$I>2\sigma(I)$]	13117	10588	10562
R_{int}	0.0283	0.0337	0.0418
parameters / restraints	890 / 48	924 / 0	807 / 266
GOF on F^2	1.046	0.960	1.026
R_1 / wR_2 [$I>2\ \sigma(I)$]	0.0384 / 0.1220	0.0379 / 0.1016	0.0539 / 0.1417
R_1 / wR_2 (all data)	0.0559 / 0.1272	0.0549 / 0.1065	0.0831 / 0.1549
max / min $\Delta\rho$[eÅ^{-3}]	0.930 / –0.541	1.234 / –1.191	2.045 / –2.093

Structure refinement details:

compound **1**: The asymmetric unit contains one cationic [Cu_3] coordination unit, consisting of three Cu, two Cl atoms and two dpmp ligands as well as the [BF_4]$^-$ anion and two CH_2Cl_2 solvent molecules. The structure solution and refinement could be done without difficulty.

compound **2**: The asymmetric unit contains one unit of the coordination compound **2** consisting of the cationic [Cu_3] complex of two dpmp ligands, three Cu and two Cl atoms coordinated to a P atom of the Mo complex **A1**. It also contains a [BF_4]$^-$ anion and two CH_2Cl_2 molecules. The solvent molecules are disordered over two positions (50:50) or three positions (49:28:23). The anion is disordered over two positions (67:33) and the minor part is refined isotropically. During the refinement process the tetrahedral geometry of the anion was restrained by SADI commands and several DFIX commands and some EADP constraints were applied to the disordered solvent molecules.

compound **3**: The asymmetric unit contains one [Cu_3] coordination unit, consisting of three Cu, two Cl atoms and two dpmp ligands coordinated to one As_2 ligand complex **A2**, two disordered CH_2Cl_2 solvent molecules and one [BF_4]$^-$ anion. One phenyl ring of the dpmp ligand is disordered over two positions with a ratio of 61 % to 39 %. The two solvent molecules are disordered over two or three positions, respectively with the occupancies of 54:46 and 50:25:25. SADI restraints as well as EADP constraints were used for the refinement of the solvent molecules.

compound **4**: With the aid of PLATON a solvent accessible area was found. The residual difference Fourier peaks exhibit a geometrical environment resembling the molecular geometry of CH_2Cl_2 molecules. Unfortunately, the refinement of disordered (and restrained) CH_2Cl_2 molecules did not lead to a satisfactory structure solution. Therefore we treated the residual electron density with the program SQUEEZE[iii] which showed a solvent accessible void. The midpoint, the size and the number of electrons in that void were refined and the contribution to the calculated structure factors of the disordered solvent is taken into account by back-Fourier transformation. The void is found around (0 0.5 0), the size is 779 A^3, and 172 e^- were detected. This electron number corresponds roughly to four CH_2Cl_2 molecules. These four CH_2Cl_2 molecules are not taken into account for the empirical formula and the calculated density, but for the analytical absorption correction and the given absorption coefficient. The disordered [BF_4]$^-$ anion was restrained with SADI commands to form a tetrahedron. Several disordered phenyl rings were fixed using the AFIX 66 command. Otherwise, the refinement was not stable or the resulting C-C bonds did not show physically correct lengths.

compound **5**: The asymmetric unit contains one cationic [Cu_3] coordination unit, consisting of three Cu, two Cl atoms and two dpmp ligands coordinated to one *cyclo*-As_5 sandwich complex **B2** as well as the [BF_4]$^-$ anion and two CH_2Cl_2 solvent molecules. The structure solution and refinement could be done without difficulty.

compound **6**:

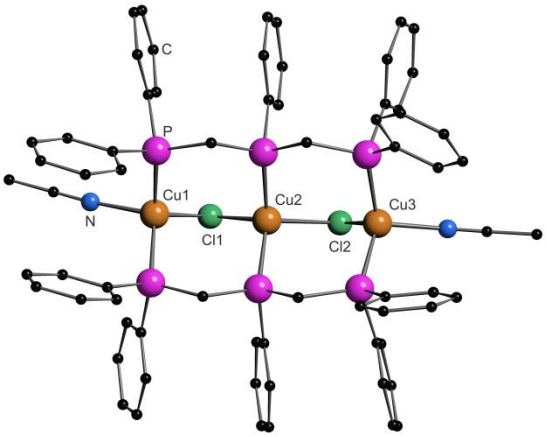


Figure 1. Crystal structure of compound 6. The BF_4^- anion, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1-Cu2 3.230(6), Cu2-Cu3 3.3239(6), Cu1-Cl1 2.3333(11), Cu2-Cl1 2.4282(10), Cu2-Cl2 2.3862(10), Cu3-Cl2 2.3612(11), Cu1–N1 2.143(4), Cu3–N3 2.065(4), Cu1-Cu2-Cu3 164.73(2).

Figure 1 shows a representation of the cationic complex in compound **6** in the solid state. The geometry of the coordination compound is in good agreement with the formerly described complex $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[ClO_4]^-\bullet H_2O$.[i] The intramolecular Cu-Cu distances are distinctly elongated compared to the novel $[Cu_3]$ coordination unit of compound **1** with vacant coordination sites on the external Cu cations.

structure solution: With the aid of PLATON a solvent accessible area was found, but it was impossible to refine any reasonable molecule from difference Fourier peaks. Therefore the midpoint, the size and the number of electrons in that void were refined and the contribution to the calculated structure factors of the disordered solvent is taken into account by back-Fourier transformation with the program SQUEEZE[iii] The void is found around (-0.192 0.052 0.173), the size is 133 A^3 and 45 e^- were detected. The void most likely contains one THF molecule. The geometry of the disordered phenyl rings on the dpmp ligand was fixed to regular hexagons (AFIX 66). The displacement parameters of these carbon atoms were restrained by ISOR commands. Otherwise, the refinement was not stable or the resulting C-C bonds did not show physically correct lengths.

Details on DFT calculations

All calculations were carried out using the TURBOMOLE program package package.[iv] The geometries were optimized using the RI-[v]BP86[vi] functional together with the def2-SVP[vii] basis set. For the geometry optimizations the Multipole Accelerated Resolution of Identity (MARI-J)[viii] approximation was used. The final energy of the molecules has been determined by single point calculations without using the RI formalism. For the calculations of the relative energies of different transformations the SCF energies has been used.

Table 3. Calculated relative energies at the BP86/def2-SVP level of theory.

Transformation	Rel. Energie ($kJ \cdot mol^{-1}$)
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{: }\eta^2\text{: }\eta^2\text{-}P_2)Mo_2(CO)_2Cp_2\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+ + [(\mu,\eta^2\text{: }\eta^2\text{-}P_2)Mo_2(CO)_2Cp_2]$	36.52
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{: }\eta^2\text{: }\eta^2\text{-}As_2)Mo_2(CO)_2Cp_2\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+ + [(\mu,\eta^2\text{: }\eta^2\text{-}As_2)Mo_2(CO)_2Cp_2]$	31.67
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{:}\eta^5\text{-}P_5)FeCp^*\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+ + [(\eta^5\text{-}P_5)FeCp^*]$	41.20
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{:}\eta^5\text{-}As_5)FeCp^*\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+ + [(\eta^5\text{-}As_5)FeCp^*]$	31.87
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{:}\eta^5\text{-}P_5)FeCp^*\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^2\text{:}\eta^5\text{-}P_5)FeCp^*\}]^+$	22.86
$[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1\text{:}\eta^5\text{-}As_5)FeCp^*\}]^+ = [Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^2\text{:}\eta^5\text{-}As_5)FeCp^*\}]^+$	16.98

Table 4. Calculated geometric parameters and energies of the model compound $[Cu_3(\mu\text{-}Cl)_2(dmmp)_2\{(\mu_3,\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}P_2)Mo_2(CO)_2Cp_2\}]^+$ (dmmp = bis(dimethylphosphino) methylenephosphane) at the BP86/def2-SVP level of theory. The Cu3-P1 distance was fixed.

Cu3-P1 (Å)	Cu3-Cu2 (Å)	Cu2-Cu1 (Å)	Tot. Energ. ($kJ \cdot mol^{-1}$)	Rel. Energ. ($kJ \cdot mol^{-1}$)
1,9260	3,7585	2,68482	-26530936,61	71,54
2,1126	3,6328	2,68962	-26530992,28	15,87
2,2653	3,5184	2,69746	-26531006,18	1,97
2,3752	3,4358	2,70449	-26531008,15	0,00
2,5650	3,2843	2,71716	-26531005,25	2,89
2,7150	3,1746	2,72719	-26531001,31	6,83
2,8650	3,0798	2,73596	-26530997,46	10,69
3,0150	3,0043	2,74162	-26530994,17	13,98
3,1650	2,9461	2,74471	-26530991,53	16,62
3,3150	2,9081	2,74984	-26530989,55	18,60
3,4650	2,8755	2,75065	-26530988,11	20,04
3,6150	2,8530	2,75154	-26530987,02	21,13

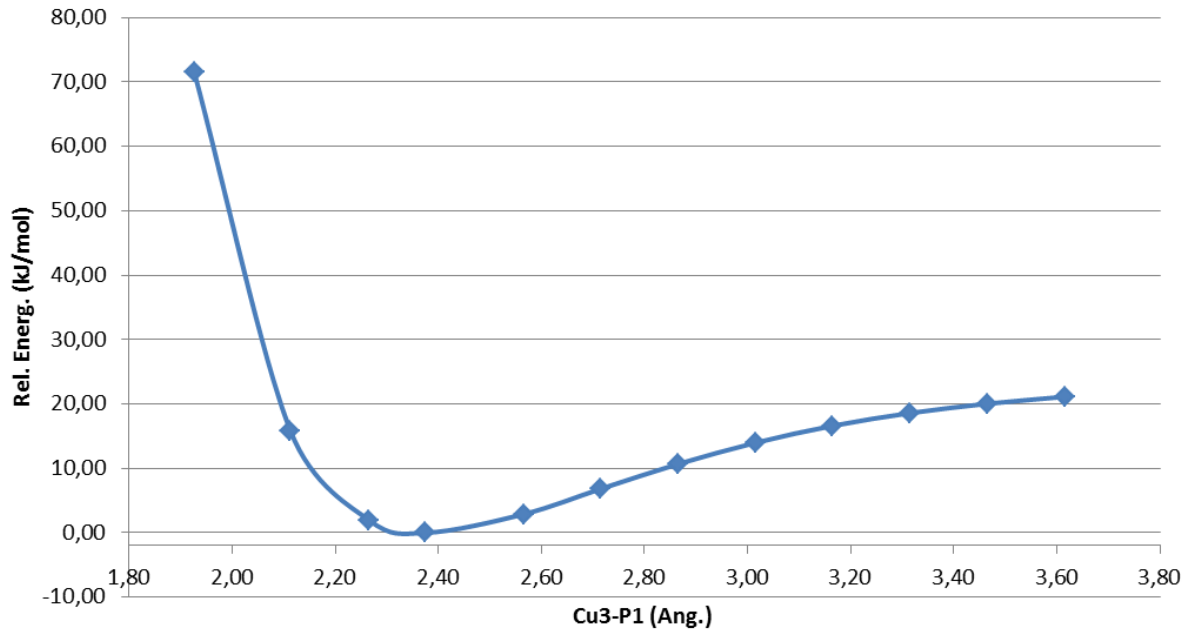


Figure 2. Variation of the relative energy of $[Cu_3(\mu\text{-}Cl)_2(dmmp)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}P_2)\ Mo_2(CO)_2Cp_2\}]^+$ (dmmp = bis(dimethylphosphino) methylenephosphane) with the Cu3-P1 distance (restrained geometry optimization). Calculated at the BP86/def2-SVP level of theory.

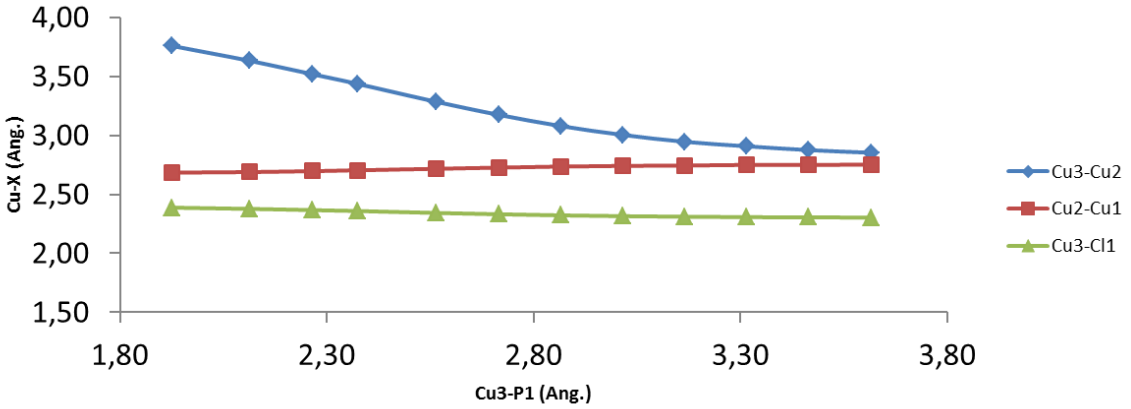


Figure 3. Variation of the Cu-X distances in $[Cu_3(\mu\text{-}Cl)_2(dmmp)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}P_2)\ Mo_2(CO)_2Cp_2\}]^+$ (dmmp = bis(dimethylphosphino) methylenephosphane) with the Cu3-P1 distance (restrained geometry optimization). Calculated at the BP86/def2-SVP level of theory.

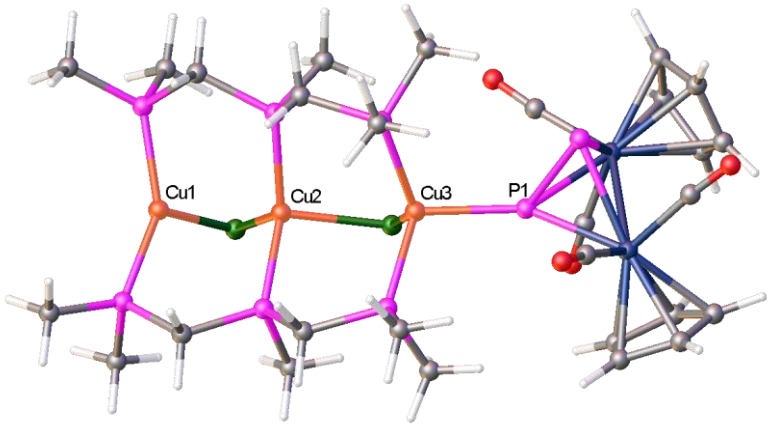
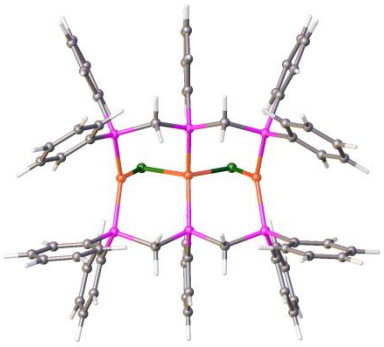


Figure 4. Geometry of the model compound $[Cu_3(\mu\text{-}Cl)_2(dmmp)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}P_2)\ Mo_2(CO)_2Cp_2\}]^+$ (Cu3-P1 distance fixed at 2.4150 Å).

Table 5. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dppm)_2]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
Cu	-2.1159590	8.0828575	32.9481763
Cu	-2.8609126	7.8239816	35.6457151
Cu	-2.8295845	8.0915136	38.4417028
P	-3.2553517	10.3004584	38.7037151
P	-0.9536586	6.9522296	39.0089463
P	-3.3705135	10.0765714	35.5763933
P	-0.8959975	6.6382898	35.9019749
P	-0.1534276	6.9497021	32.8840095
P	-2.4718886	10.2885158	32.5779938
Cl	-3.9308795	6.8602930	33.6461819
Cl	-4.4165747	6.8787333	37.3072967
C	0.4638879	6.9643450	34.6481629
C	-0.1780500	5.1738200	32.3856416
C	1.2735632	7.6160546	31.9138074
C	-2.5312963	11.1132842	34.2553020
C	-1.1853581	11.2628779	31.6838023
C	-4.0465044	10.7630411	31.7362458
H	1.3295863	6.2824073	34.7858311
H	0.8023188	8.0022592	34.8507877
C	1.0146067	4.4373936	32.2035640
C	-1.4245846	4.5528398	32.1623272
C	1.2937023	7.3590212	30.5222460
C	2.2949398	8.4142762	32.4705949
H	-1.4726772	11.2176041	34.5752228
H	-2.9817856	12.1264590	34.2008316
C	-0.6030313	10.6615698	30.5461381
C	-0.7801609	12.5644409	32.0535676
C	-5.0870664	9.8102826	31.6860224
C	-4.2243667	12.0263123	31.1301146
C	0.0976414	6.9586236	37.4634042
C	-1.0973383	4.8059806	35.8740058
H	1.9937088	4.9176953	32.3573843
C	0.9561629	3.0946962	31.8026322
C	-1.4749475	3.2073787	31.7587011



H	-2.3547324	5.1224510	32.3175008
H	0.5099105	6.7335632	30.0662394
C	2.3186669	7.8752429	29.7157825
C	3.3189440	8.9329879	31.6588920
H	2.3123292	8.6370675	33.5478126
C	-2.8859094	11.1167839	37.0621593
C	-5.1638144	10.4485985	35.3485210
H	-0.8941390	9.6380596	30.2616059
C	0.3491102	11.3538298	29.7830079
C	0.1825724	13.2510375	31.2938019
H	-1.2149679	13.0596508	32.9347658
H	-4.9472861	8.8200815	32.1488653
C	-6.2979184	10.1286393	31.0488779
C	-5.4364843	12.3353142	30.4937013
H	-3.4102617	12.7672029	31.1381569
H	0.4848354	7.9935066	37.3547737
H	0.9641914	6.2696956	37.5532680
C	-2.3949601	4.2749497	35.7241942
C	0.0034870	3.9299861	35.9992439
H	1.8877817	2.5264861	31.6576949
C	-0.2887302	2.4791891	31.5770532
H	-2.4505155	2.7294721	31.5829388
H	2.3256118	7.6534171	28.6375763
C	3.3361947	8.6638350	30.2817153
H	4.1121782	9.5468739	32.1120615
H	-3.3292328	12.1326263	36.9976452
H	-1.7802516	11.2144746	37.0187151
C	-5.6501457	11.7738918	35.2954045
C	-6.0672031	9.3728529	35.2244528
H	0.7917898	10.8728604	28.8981800
C	0.7442282	12.6501080	30.1554965
H	0.4899222	14.2651877	31.5917139
H	-7.1048152	9.3811534	31.0134022
C	-6.4745847	11.3878795	30.4529304
H	-5.5673477	13.3195209	30.0183597
C	-1.1163989	5.1786031	39.4877903
C	0.1799019	7.6156957	40.3121640
H	-3.2542912	4.9536874	35.6265911
C	-2.5853002	2.8831828	35.7008644
C	-0.1925771	2.5417821	35.9747580
H	1.0270262	4.3209523	36.1171068
H	-0.3308819	1.4276731	31.2541815
H	4.1432042	9.0640649	29.6496454
C	-2.2271703	11.2704118	39.8893675
C	-4.9876703	10.7878416	39.1209893
H	-4.9656037	12.6324508	35.3899695
C	-7.0198286	12.0185086	35.1211504
C	-7.4387375	9.6237258	35.0499924
H	-5.6936436	8.3396599	35.2647305
H	1.4943708	13.1917360	29.5595759
H	-7.4212619	11.6309901	29.9465844
C	-2.3869562	4.5716522	39.4057543
C	-0.0109117	4.4303229	39.9525962
C	1.2926325	8.4373472	40.0340669
C	-0.1384991	7.3366668	41.6625711
H	-3.6017057	2.4776702	35.5838889
C	-1.4887475	2.0166479	35.8253874

H	0.6704542	1.8659649	36.0726354
C	-1.9438389	10.6652828	41.1336672
C	-1.7417947	12.5720944	39.6342077
C	-5.3033301	12.0522357	39.6654491
C	-6.0145787	9.8436678	38.9036079
H	-7.3895115	13.0543431	35.0811550
C	-7.9166443	10.9421024	34.9983321
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H	-3.2454878	5.1498709	39.0286383
C	-2.5484297	3.2288917	39.7888846
C	-0.1793731	3.0903960	40.3308812
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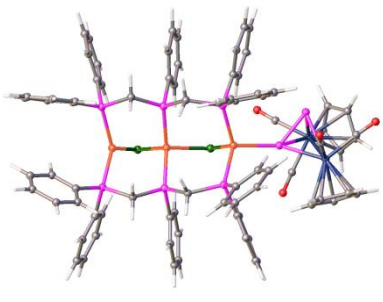
H	1.5694776	8.6794734	38.9972139
C	2.0771151	8.9557255	41.0789917
C	0.6477342	7.8537376	42.7028889
H	-0.9995699	6.6936209	41.9039202
H	-1.6404164	0.9265279	35.8063876
H	-2.2962713	9.6412466	41.3343474
C	-1.2088340	11.3542685	42.1099681
C	-0.9955345	13.2552343	40.6098198
H	-1.9452414	13.0698429	38.6741415
H	-4.5079874	12.7863261	39.8661961
C	-6.6347099	12.3711692	39.9745420
C	-7.3448659	10.1720750	39.2134137
H	-5.7698642	8.8522738	38.4894984
H	-8.9915520	11.1360708	34.8618032
H	-3.5428354	2.7618856	39.7252189
C	-1.4490963	2.4893262	40.2523173
H	0.6835815	2.5128821	40.6962503
H	2.9469247	9.5874024	40.8426113
C	1.7599908	8.6643028	42.4147265
H	0.3929411	7.6145385	43.7467519
H	-0.9984638	10.8702608	43.0752279
C	-0.7328045	12.6507303	41.8499314
H	-0.6230336	14.2695353	40.3996179
H	-6.8738556	13.3562961	40.4035718
C	-7.6568179	11.4325615	39.7482061
H	-8.1403726	9.4314224	39.0411712
H	-1.5796039	1.4398767	40.5578016
H	2.3803337	9.0644336	43.2308367
H	-0.1523310	13.1897569	42.6139390
H	-8.6990147	11.6834565	39.9983469

Table 6. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dppm)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}P_2)\ Mo_2(CO)_2Cp_2\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
Mo	3.1585524	11.7612154	15.0617233
Mo	5.0072623	13.1846595	13.0605651
Cu	6.3211495	16.7366537	23.1566111
Cu	5.7586566	15.7213896	20.6914785
Cu	5.3623583	15.3264710	17.1990281
Cl	4.9600813	14.0491086	19.1529827
Cl	5.3979221	14.6437353	22.8797183
P	4.6303173	13.8777016	15.4302444



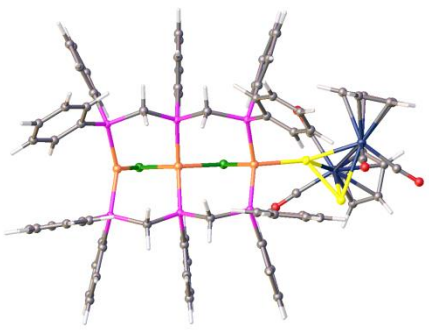
P	2.8722294	14.1138027	14.2562104
P	4.8616997	18.4686090	23.3257551
P	4.2635974	17.4236455	20.4587132
P	4.0660366	17.2546977	17.2602183
P	7.6694242	15.6026189	17.0710147
P	7.9984581	15.7269484	20.2761302
P	8.5816684	16.9086251	23.1005727
O	2.7054079	12.8152695	10.9486733
O	5.0590364	16.1594745	12.0670062
O	2.0559974	12.4777738	17.9089958
O	5.7108420	10.5641239	16.4519486
C	6.3942710	11.2231644	13.1329413
C	6.1286014	11.5717720	11.7711378
C	6.7023381	12.8643092	11.5187301
C	7.3172787	13.3128926	12.7437757
C	7.1222635	12.3019163	13.7369328
C	3.5157168	12.9591603	11.7801496
C	4.9979705	15.0712123	12.4917514
C	1.3894593	11.1735266	13.5617004
C	2.5145973	10.3487432	13.2237486
C	2.8315806	9.5403354	14.3599471
C	1.8971884	9.8495994	15.4055035
C	1.0034850	10.8651525	14.9027090
C	2.5235828	12.2916980	16.8573150
C	4.7994310	11.0804932	15.9311928
C	4.5012601	18.9338124	21.5520590
C	4.2967830	18.3019642	18.8017552
C	8.5266340	16.3275060	18.5794015
C	9.0688528	16.8869275	21.2945965
C	5.3788871	20.0652317	24.1051975
C	5.3432559	20.1440719	25.5178042
C	5.7639936	21.3071062	26.1791914
C	6.2359316	22.4088375	25.4436071
C	6.2850582	22.3365056	24.0430122
C	5.8605959	21.1733988	23.3769735
C	3.2182694	18.1677695	24.1094014
C	2.8975925	16.8563436	24.5177573
C	1.6674852	16.5994841	25.1477824
C	0.7561761	17.6434474	25.3711895
C	1.0708887	18.9518220	24.9604453
C	2.2973828	19.2163544	24.3338753
C	2.5029863	16.9645719	20.7482458
C	2.2278060	15.6353495	21.1312909
C	0.9057183	15.2395240	21.3938526
C	-0.1444555	16.1626230	21.2746060
C	0.1248766	17.4881272	20.8882918
C	1.4428206	17.8891142	20.6266062
C	2.2332203	17.0310102	17.1896355
C	1.7072576	15.7861458	17.5893319
C	0.3201081	15.5661951	17.5649318
C	-0.5473981	16.5821386	17.1319549
C	-0.0272598	17.8265474	16.7342113
C	1.3575369	18.0541380	16.7640712
C	4.3591539	18.5017710	15.9218379
C	5.0427304	19.7217831	16.1123991
C	5.2529861	20.5998169	15.0346001
C	4.7823202	20.2735180	13.7535541

C	4.1070608	19.0569363	13.5514062
C	3.9022956	18.1756459	14.6229772
C	8.2727737	16.7474001	15.7482341
C	9.5032081	17.4421766	15.7937251
C	9.8889951	18.2766290	14.7312236
C	9.0550964	18.4257861	13.6100328
C	7.8264892	17.7466755	13.5585825
C	7.4358561	16.9199379	14.6243916
C	8.6232282	14.0396825	16.7890809
C	9.8221103	13.9887736	16.0446345
C	10.5020246	12.7696365	15.8843637
C	9.9939504	11.5952763	16.4659475
C	8.7969722	11.6396768	17.2006781
C	8.1062608	12.8532197	17.3554923
C	8.8385762	14.0965336	20.4823893
C	10.2174746	13.9159046	20.2379441
C	10.8109286	12.6596316	20.4289229
C	10.0326699	11.5731920	20.8675717
C	8.6614542	11.7470848	21.1117870
C	8.0621442	13.0033722	20.9201366
C	9.5568733	15.5565226	23.8977074
C	10.9259663	15.7003206	24.2134005
C	11.6174630	14.6496202	24.8356506
C	10.9488722	13.4535869	25.1516546
C	9.5862764	13.3099949	24.8441878
C	8.8863542	14.3576063	24.2224488
C	9.3847495	18.4458630	23.7324722
C	10.4405162	19.1155284	23.0755255
C	11.0168127	20.2642809	23.6450359
C	10.5514211	20.7514775	24.8770932
C	9.4988564	20.0927966	25.5357747
C	8.9141078	18.9530608	24.9640435
H	6.1260196	10.2805011	13.6208509
H	5.6150519	10.9448353	11.0319805
H	6.7149805	13.3873454	10.5551810
H	7.8675902	14.2508461	12.8838522
H	7.4915959	12.3306390	14.7683859
H	0.8951032	11.8874394	12.8934867
H	3.0122024	10.3123003	12.2495382
H	3.6224288	8.7821669	14.4115236
H	1.8403288	9.3628717	16.3862037
H	0.1525623	11.2981993	15.4419121
H	5.4181095	19.4317418	21.1722665
H	3.6554661	19.6491948	21.4714230
H	3.5789825	19.1503139	18.7812472
H	5.3232565	18.7216376	18.7406340
H	9.6272190	16.2257583	18.4691560
H	8.2823765	17.4112009	18.5624057
H	10.1492543	16.6724183	21.1550569
H	8.8621589	17.9108395	20.9166030
H	4.9658686	19.2931267	26.1068423
H	5.7163056	21.3549099	27.2779643
H	6.5608681	23.3233401	25.9623991
H	6.6500780	23.1942675	23.4577352
H	5.9036609	21.1492954	22.2779795
H	3.6091630	16.0361881	24.3299347
H	1.4246946	15.5746484	25.4670418

H	-0.2036864	17.4406077	25.8705100
H	0.3586524	19.7725493	25.1363194
H	2.5450789	20.2469433	24.0346685
H	3.0535073	14.9143159	21.2229079
H	0.7003568	14.2006594	21.6934208
H	-1.1798779	15.8516810	21.4823667
H	-0.6968142	18.2136295	20.7907010
H	1.6339796	18.9311008	20.3238508
H	2.3887096	14.9942980	17.9337395
H	-0.0768620	14.5914545	17.8846341
H	-1.6336645	16.4057156	17.1022786
H	-0.7040160	18.6249097	16.3926417
H	1.7561081	19.0272800	16.4383866
H	5.4160611	20.0108056	17.1055474
H	5.7837378	21.5492178	15.2038792
H	4.9399013	20.9659650	12.9127671
H	3.7389894	18.7860995	12.5508207
H	3.3688567	17.2270445	14.4506649
H	10.1764499	17.3384318	16.6580442
H	10.8497556	18.8119110	14.7800662
H	9.3605933	19.0799016	12.7791628
H	7.1549451	17.8663660	12.6959430
H	6.4600316	16.4112404	14.5977985
H	10.2248473	14.8997197	15.5766593
H	11.4328320	12.7381290	15.2972442
H	10.5286610	10.6415633	16.3382068
H	8.3831939	10.7235981	17.6459831
H	7.1589690	12.8829651	17.9176049
H	10.8452227	14.7540057	19.8941412
H	11.8863680	12.5275329	20.2359347
H	10.5011474	10.5886943	21.0199249
H	8.0478963	10.9007852	21.4563437
H	6.9879507	13.1429373	21.1122271
H	11.4522711	16.6411990	23.9901493
H	12.6831950	14.7693899	25.0840781
H	11.4922101	12.6344589	25.6472513
H	9.0571270	12.3783232	25.0955839
H	7.8156683	14.2468665	23.9851592
H	10.8291942	18.7452508	22.1149820
H	11.8393288	20.7770205	23.1231263
H	11.0071001	21.6484794	25.3231558
H	9.1223814	20.4739830	26.4966026
H	8.0762309	18.4528821	25.4749273

Table 7. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dppm)_2\{(\mu_3,\eta^1{:}\eta^2{:}\eta^2\text{-}As_2)\ Mo_2(CO)_2Cp_2\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
Cu	11.2121151	6.3276361	12.5625427
Cu	10.8345364	6.0068547	9.1790979
Cu	10.2635433	5.0269715	6.6898561
Cl	11.1923836	7.1102753	6.9989365
Cl	11.6615229	7.6913814	10.6960646
P	12.3376335	4.3027605	9.3752623
P	8.5900171	6.0093069	9.5889550
P	11.7213871	3.2969870	6.4961381



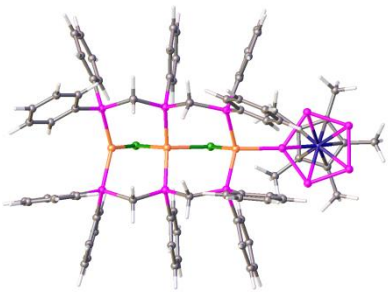
P	8.0026664	4.8690244	6.7454184
P	12.5462711	4.4447266	12.5618501
P	8.9232767	6.0956614	12.7812701
Mo	11.6269015	8.6390477	16.9162425
Mo	13.4717269	10.0922691	14.8718742
As	11.9254997	7.9065373	14.4346899
As	13.8751967	7.6565642	15.7289647
C	9.5015506	9.5124102	16.2593714
H	9.1002464	9.4581579	15.2408870
C	10.2502300	10.6042591	16.8119701
C	9.3277649	8.5325688	17.2885577
H	10.5108342	11.5295969	16.2882805
C	10.5481207	10.2948389	18.1772177
C	9.9728831	9.0141771	18.4841642
H	8.7683684	7.5946102	17.1911488
C	13.1270599	8.8568536	18.1865174
C	11.6108515	6.7443491	17.4511749
H	11.0810603	10.9413463	18.8850210
H	9.9811953	8.5199719	19.4627430
O	13.9322738	9.0143535	19.0225941
O	11.5206206	5.6469517	17.8507361
C	13.6945189	12.3192280	15.5817709
C	14.6489674	12.0541330	14.5413529
C	15.5809976	11.0773689	15.0481668
C	15.2008920	10.7494640	16.3875277
C	14.0387944	11.5234351	16.7192830
C	11.8358336	10.7230754	13.9592075
C	14.1622290	9.5247151	13.1108189
C	12.3284186	3.3996298	11.0191608
C	14.3733791	4.7008184	12.6449356
C	12.2593838	3.2027231	13.9051629
C	8.0478805	5.3927169	11.2758317
C	8.3363740	4.9475690	14.1072255
C	7.9919540	7.6643192	13.1001193
H	12.8726687	13.0433789	15.5261506
H	14.6910341	12.5439869	13.5615437
H	16.4537963	10.6834432	14.5137877
H	15.7251686	10.0621423	17.0608025
H	13.5348328	11.5356883	17.6906591
O	10.9282909	11.2286991	13.4176219
O	14.6617293	9.3126655	12.0771920
H	11.3096402	2.9621466	11.0838201
H	13.0614604	2.5643028	11.0261471
C	15.2605257	3.6885851	13.0729107
C	14.8828793	5.9572056	12.2587187
C	11.6269457	1.9560935	13.7113362
C	12.6682375	3.5608520	15.2115739
H	8.2801240	4.3062765	11.2815585
H	6.9487703	5.5075042	11.3876299
C	7.1217752	4.2263158	14.0556276
C	9.1629602	4.8076325	15.2433199
C	6.7935820	7.7091036	13.8458393
C	8.5222470	8.8583065	12.5631527
C	12.0935110	2.8089552	8.2612950
C	14.0951412	4.7708876	9.0809468
H	14.8733000	2.7080481	13.3902659
C	16.6414099	3.9365992	13.1155203

C	16.2665810	6.1974085	12.2967443
H	14.1932654	6.7436853	11.9165844
H	11.2936735	1.6410718	12.7118542
C	11.4182998	1.0844303	14.7948138
C	12.4643973	2.6868264	16.2890247
H	13.1614438	4.5306313	15.3862046
C	7.5163352	4.8694157	8.5516955
C	7.7624100	7.6485453	9.4037340
H	6.4565032	4.3059085	13.1827043
C	6.7415060	3.3962523	15.1237165
C	8.7768303	3.9865803	16.3147454
H	10.1273929	5.3371925	15.2789370
H	6.3817190	6.7907593	14.2910614
C	6.1262787	8.9308149	14.0352760
C	7.8447667	10.0752487	12.7483647
H	9.4677633	8.8322326	11.9977911
H	12.9411353	2.0941518	8.3259543
H	11.1804294	2.3040978	8.6408912
C	15.1583266	3.8490292	9.1974519
C	14.3661637	6.1031960	8.7060066
H	17.3273165	3.1465568	13.4581599
C	17.1456615	5.1912199	12.7293814
H	16.6503921	7.1811736	11.9891455
H	10.9279589	0.1138862	14.6235568
C	11.8393238	1.4440489	16.0841168
H	12.7928788	2.9843075	17.2958245
H	7.7168412	3.8393044	8.9159492
H	6.4372069	5.0884311	8.6939218
C	6.3845191	7.8346300	9.6503333
C	8.5466070	8.7432735	8.9842633
H	5.7933104	2.8394943	15.0699076
C	7.5642376	3.2795692	16.2567398
H	9.4393651	3.8943785	17.1876950
H	5.1951918	8.9578060	14.6221637
C	6.6475793	10.1137381	13.4830538
H	8.2692528	10.9974827	12.3266389
C	11.1976824	1.7104310	5.7004101
C	13.3601358	3.6080698	5.7072598
C	7.0347692	6.2376600	5.9679408
C	7.1916557	3.3444239	6.0938267
H	14.9705491	2.8044435	9.4933382
C	16.4752120	4.2559942	8.9397252
C	15.6872267	6.5048928	8.4470818
H	13.5385261	6.8223432	8.6179617
H	18.2288474	5.3839032	12.7691142
H	11.6820101	0.7570978	16.9294338
H	5.7506238	6.9954955	9.9800492
C	5.7998679	9.0978809	9.4795601
C	7.9560006	10.0066408	8.8130099
H	9.6200413	8.6000880	8.7910403
H	7.2625656	2.6296413	17.0922580
H	6.1228643	11.0696175	13.6339659
C	10.6938453	0.6048002	6.4175669
C	11.2461560	1.6389118	4.2878285
C	14.2838722	2.5639837	5.4735503
C	13.6749028	4.9229118	5.3053912
C	5.6651842	6.1052688	5.6493684

C	7.7110712	7.4384024	5.6624423
C	6.1263170	2.6770642	6.7375980
C	7.6661146	2.8454916	4.8603700
H	17.2992308	3.5326933	9.0340186
C	16.7405054	5.5848767	8.5623337
H	15.8893746	7.5463469	8.1544436
H	4.7252415	9.2341629	9.6741497
C	6.5859368	10.1860087	9.0593761
H	8.5758094	10.8542926	8.4833624
H	10.6393311	0.6236327	7.5161965
C	10.2610359	-0.5489945	5.7410165
C	10.8163408	0.4851869	3.6158527
H	11.6404659	2.4878539	3.7071632
H	14.0408645	1.5307698	5.7675671
C	15.5071902	2.8364019	4.8441889
C	14.9016386	5.1876442	4.6720545
H	12.9617138	5.7396338	5.5015528
H	5.1342658	5.1634831	5.8572716
C	4.9788922	7.1690304	5.0437414
C	7.0162734	8.4991195	5.0574112
H	8.7822288	7.5403039	5.9014437
H	5.7346533	3.0410166	7.6993712
C	5.5444329	1.5386628	6.1532430
C	7.0757377	1.7162279	4.2737478
H	8.5114106	3.3437076	4.3598729
H	17.7751648	5.9008761	8.3585411
H	6.1244230	11.1761524	8.9233056
H	9.8789034	-1.4049984	6.3178613
C	10.3228801	-0.6142598	4.3405107
H	10.8742186	0.4428731	2.5173488
H	16.2218823	2.0193085	4.6615307
C	15.8157430	4.1481629	4.4395298
H	15.1396967	6.2151014	4.3577180
H	3.9127742	7.0581271	4.7928953
C	5.6531146	8.3669103	4.7473581
H	7.5499082	9.4321967	4.8212069
H	4.7144836	1.0275329	6.6648490
C	6.0137048	1.0598218	4.9193375
H	7.4552657	1.3414043	3.3116276
H	9.9909805	-1.5214964	3.8134412
H	16.7731215	4.3571548	3.9379961
H	5.1137269	9.1965089	4.2650501
H	5.5536278	0.1709402	4.4616840

Table 8. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^5\text{-}P_5)FeCp^*\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
Cu	-2.3685675	7.8098217	32.2669085
Cu	-3.0471145	7.6804229	35.7086250
Cu	-2.9389543	8.0115905	38.4135530
P	-3.2878347	10.2405673	38.6365186
P	-1.0316529	6.9101278	38.9636524
P	-3.4227031	9.9227877	35.5347410
P	-1.0458085	6.6018133	35.8689501
P	-0.2855523	6.9261989	32.7807367



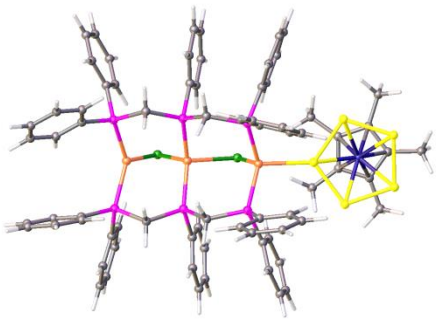
P	-2.5418764	10.1180468	32.4480970
Cl	-4.0043039	6.7973566	33.6710189
Cl	-4.5898962	6.7655443	37.3978594
Fe	-4.2221231	6.1726661	28.4167894
P	-2.4090790	5.9580609	26.8604618
P	-1.9660774	5.6166433	28.9382713
P	-2.8483163	7.2511382	30.0361958
P	-3.9306122	8.5283320	28.6778499
P	-3.6140929	7.7360440	26.7031813
C	-4.9842400	4.2255406	28.2284168
C	-5.6555553	5.1117639	27.3030940
C	-5.2085424	4.7233123	29.5670970
C	-4.2677608	2.9586982	27.8699256
C	-6.2935759	6.1579240	28.0715205
C	-5.7613296	4.9197519	25.8202710
C	-6.0181978	5.9172009	29.4701099
C	-4.7805669	4.0539890	30.8373455
H	-4.9786748	2.1039730	27.8655115
H	-3.4637469	2.7232491	28.5937974
H	-3.8069703	3.0165113	26.8649378
C	-7.1688046	7.2438261	27.5221800
H	-6.6514230	4.2991395	25.5784490
H	-4.8720249	4.4063283	25.4065259
H	-5.8696444	5.8836532	25.2865623
C	-6.5731942	6.6973317	30.6219350
H	-4.6659371	4.7761363	31.6690882
H	-3.8188759	3.5207249	30.7103106
H	-5.5414975	3.3039720	31.1457744
H	-6.8674539	7.5367657	26.4979443
H	-7.1386459	8.1531259	28.1531856
H	-8.2248797	6.8993886	27.4766298
H	-7.5699706	6.2946895	30.9066537
H	-6.7055579	7.7649525	30.3619626
H	-5.9208301	6.6410187	31.5150074
C	0.2292512	7.0781220	34.5788165
C	-0.0431245	5.1265326	32.4374904
C	1.1539021	7.6941559	31.9035776
C	-2.4754413	10.8204585	34.1885695
C	-1.2143019	11.0981772	31.6079265
C	-4.1013240	10.8511263	31.7755845
H	1.1891367	6.5419409	34.7410799
H	0.4067172	8.1597077	34.7586698
C	1.2349566	4.5611837	32.2350070
C	-1.1854698	4.3012779	32.3902535
C	1.2358046	7.4935068	30.5050526
C	2.1385987	8.4853225	32.5322900
H	-1.4100997	10.7528197	34.4965703
H	-2.7587543	11.8943675	34.1718600
C	-0.7791062	10.6391176	30.3441843
C	-0.6422030	12.2767374	32.1369851
C	-5.2845479	10.0896419	31.8852973
C	-4.1462368	12.1241769	31.1682090
C	-0.0097339	6.9442711	37.3987557
C	-1.1344660	4.7616462	35.8240893
H	2.1324821	5.1986450	32.2529903
C	1.3651140	3.1853993	31.9892487
C	-1.0475937	2.9229611	32.1575047

H	-2.1806333	4.7464696	32.5450900
H	0.4746137	6.8852695	29.9909305
C	2.2853583	8.0534134	29.7632147
C	3.1842341	9.0542818	31.7834286
H	2.1113279	8.6647999	33.6168470
C	-2.8828273	10.9999315	36.9759971
C	-5.1851929	10.4122227	35.2924441
H	-1.2058531	9.7164391	29.9212540
C	0.1893346	11.3512287	29.6207398
C	0.3373598	12.9806246	31.4155122
H	-0.9583138	12.6671941	33.1153351
H	-5.2459723	9.0877030	32.3406734
C	-6.5020227	10.6120438	31.4205267
C	-5.3644336	12.6329268	30.6888235
H	-3.2264559	12.7179762	31.0560942
H	0.3464023	7.9899554	37.2868162
H	0.8765503	6.2778270	37.4635131
C	-2.4135302	4.1683109	35.7877988
C	0.0142557	3.9412797	35.8520336
H	2.3634196	2.7526818	31.8217859
C	0.2243042	2.3646173	31.9513159
H	-1.9416195	2.2818350	32.1341019
H	2.3377065	7.8747105	28.6783708
C	3.2642153	8.8368970	30.3998104
H	3.9451820	9.6659083	32.2918855
H	-3.2816723	12.0316569	36.8788900
H	-1.7738896	11.0466342	36.9314721
C	-5.5850678	11.7563790	35.1280650
C	-6.1601903	9.3929595	35.2972502
H	0.5102027	10.9818378	28.6353320
C	0.7517923	12.5228950	30.1545602
H	0.7731640	13.8973475	31.8416665
H	-7.4239501	10.0208371	31.5274083
C	-6.5440696	11.8807968	30.8184179
H	-5.3896284	13.6226004	30.2073651
C	-1.1500438	5.1340262	39.4485360
C	0.1095667	7.5925348	40.2505832
H	-3.3082668	4.8084073	35.7681759
C	-2.5385490	2.7689436	35.7836473
C	-0.1163531	2.5451529	35.8449450
H	1.0233797	4.3829193	35.8763509
H	0.3287786	1.2862353	31.7564977
H	4.0883219	9.2757918	29.8172790
C	-2.2324875	11.2035141	39.8051316
C	-5.0006666	10.8019118	39.0426601
H	-4.8419675	12.5700820	35.1177838
C	-6.9412604	12.0761292	34.9699773
C	-7.5181188	9.7186947	35.1410941
H	-5.8496355	8.3455574	35.4282328
H	1.5147886	13.0785349	29.5885195
H	-7.4976526	12.2831232	30.4434545
C	-2.4157540	4.5122448	39.4199419
C	-0.0192095	4.4016107	39.8757910
C	1.2139985	8.4197617	39.9565783
C	-0.1923692	7.3183228	41.6057165
H	-3.5403462	2.3136431	35.7608766
C	-1.3938981	1.9574666	35.8125844

H	0.7833289	1.9117637	35.8654970
C	-2.0095369	10.6375416	41.0799924
C	-1.6695058	12.4642419	39.5080368
C	-5.2756611	12.1087844	39.5021987
C	-6.0527452	9.8696119	38.9149871
H	-7.2440048	13.1261678	34.8402280
C	-7.9101055	11.0565932	34.9776049
H	-8.2728700	8.9175247	35.1513607
H	-3.2943965	5.0785673	39.0715299
C	-2.5473111	3.1710687	39.8200044
C	-0.1574755	3.0627322	40.2697097
H	0.9706750	4.8826042	39.9189024
H	1.4785595	8.6570895	38.9154497
C	2.0056317	8.9492367	40.9905565
C	0.6010323	7.8460099	42.6350008
H	-1.0467520	6.6709125	41.8590852
H	-1.4933629	0.8610898	35.8113237
H	-2.4240304	9.6445966	41.3157290
C	-1.2575435	11.3258007	42.0435980
C	-0.9062280	13.1460959	40.4715169
H	-1.8253207	12.9313559	38.5240069
H	-4.4593975	12.8360098	39.6323464
C	-6.5915759	12.4801263	39.8178644
C	-7.3676187	10.2494396	39.2326665
H	-5.8389091	8.8469518	38.5638961
H	-8.9745408	11.3102854	34.8571388
H	-3.5382803	2.6928175	39.7993001
C	-1.4225610	2.4472589	40.2457116
H	0.7255476	2.4975069	40.6051820
H	2.8685568	9.5856050	40.7417323
C	1.7044896	8.6628449	42.3310108
H	0.3586012	7.6110048	43.6827829
H	-1.0955155	10.8730730	43.0330813
C	-0.7035206	12.5815758	41.7411933
H	-0.4730086	14.1283664	40.2279578
H	-6.7991974	13.4987452	40.1799335
C	-7.6387995	11.5512197	39.6838942
H	-8.1831242	9.5172440	39.1323994
H	-1.5291255	1.3989265	40.5641857
H	2.3304563	9.0716623	43.1385056
H	-0.1094712	13.1195623	42.4954540
H	-8.6686741	11.8431103	39.9406884

Table 9. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^1{:}\eta^5\text{-}As_5)FeCp^*\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
As	0.8516740	7.0375531	26.4903572
As	-0.1556927	5.2124918	27.6094264
As	0.3470778	5.4591975	29.8994652
As	1.7009106	7.3722308	30.1688944
As	2.0591457	8.3425368	28.0506521
Cu	0.3891339	7.7287004	24.1310954
Cu	1.2339149	7.6344127	20.8014881
Cu	1.2576189	8.0125325	18.0921443
Fe	2.2369461	5.8127276	28.2182704



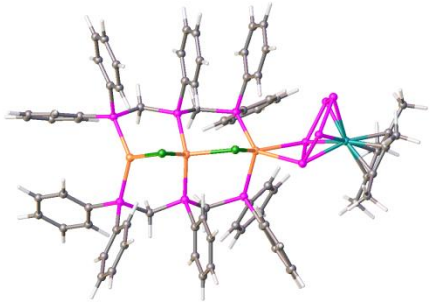
Cl	2.1067386	6.6972010	22.8548698
Cl	2.8598214	6.7557936	19.1675095
P	-1.6705455	6.8499270	23.5652397
P	-0.7510305	6.5476869	20.5163452
P	-0.6093761	6.9055777	17.4280720
P	1.6041809	10.2467661	17.9301256
P	1.5993656	9.8759504	21.0304963
P	0.6097142	10.0271267	24.0749944
C	4.0255682	5.5893370	27.1365740
C	4.3161386	5.7376118	28.5448656
C	3.6657622	4.6569937	29.2523605
C	2.9730543	3.8410759	28.2798991
C	3.1952216	4.4171431	26.9728312
C	4.6036797	6.4165403	26.0284748
C	5.2393446	6.7533009	29.1486690
C	3.8024616	4.3552391	30.7148144
C	2.2643024	2.5500618	28.5618848
C	2.7657700	3.8219090	25.6659417
C	-2.0978654	6.9891677	21.7433685
C	-1.7084560	6.9086898	18.9397474
C	1.1221668	10.9749140	19.5837892
C	0.5920148	10.7534884	22.3462768
C	-3.1527917	7.6213975	24.3638680
C	-4.2390989	8.1838173	23.6596550
C	-5.3279749	8.7414852	24.3533549
C	-5.3506099	8.7374262	25.7562018
C	-4.2727538	8.1802353	26.4662519
C	-3.1795375	7.6350633	25.7781298
C	-1.9182927	5.0510620	23.9130454
C	-3.1955993	4.4936635	24.1391283
C	-3.3294446	3.1180476	24.3858587
C	-2.1935340	2.2902209	24.4026047
C	-0.9216227	2.8417056	24.1770077
C	-0.7790263	4.2193845	23.9435051
C	-0.6582142	4.7068988	20.5385699
C	-1.8039324	3.8861099	20.4543091
C	-1.6727841	2.4900509	20.4531192
C	-0.3971900	1.9027459	20.5329811
C	0.7446154	2.7145807	20.6165047
C	0.6188296	4.1139475	20.6211502
C	-0.4534718	5.1380418	16.9228217
C	-1.5568523	4.4044994	16.4306073
C	-1.3897803	3.0726896	16.0241958
C	-0.1227258	2.4655526	16.0999779
C	0.9748041	3.1905530	16.5898496
C	0.8140561	4.5245537	17.0030652
C	-1.6901164	7.5997457	16.0960537
C	-2.8171900	8.4106157	16.3464395
C	-3.5600782	8.9501322	15.2819075
C	-3.1870512	8.6901283	13.9542039
C	-2.0606430	7.8896334	13.6940068
C	-1.3157443	7.3520605	14.7539581
C	0.5989840	11.2279754	16.7327269
C	0.0174154	12.4807707	17.0275404
C	-0.7042824	13.1780321	16.0432618
C	-0.8468529	12.6367976	14.7553893
C	-0.2742738	11.3888749	14.4550263

C	0.4367585	10.6854834	15.4386141
C	3.3315290	10.8206149	17.6121524
C	3.6221713	12.1379939	17.1940628
C	4.9494875	12.5193471	16.9451837
C	5.9928950	11.5902017	17.1049772
C	5.7064075	10.2780599	17.5147365
C	4.3800564	9.8882172	17.7655217
C	3.3491430	10.3596938	21.3579905
C	3.7405231	11.7001991	21.5668149
C	5.0889623	12.0163839	21.7863982
C	6.0582703	10.9972595	21.7963791
C	5.6743882	9.6630891	21.5899088
C	4.3241865	9.3406645	21.3724987
C	2.1649443	10.7191418	24.7974049
C	2.2278140	12.0095926	25.3663298
C	3.4402205	12.4913361	25.8856360
C	4.5965845	11.6941829	25.8348231
C	4.5368552	10.4094715	25.2699385
C	3.3240611	9.9149538	24.7631630
C	-0.7095028	11.0195607	24.9147883
C	-1.0184990	10.6720360	26.2502411
C	-1.9782170	11.3959174	26.9725862
C	-2.6596884	12.4670434	26.3693184
C	-2.3714311	12.8112951	25.0397439
C	-1.3999499	12.0964529	24.3169350
H	4.7575009	7.4671273	26.3420992
H	3.9563121	6.4201511	25.1298492
H	5.5934782	6.0079102	25.7276606
H	6.2820894	6.3668778	29.1547176
H	4.9649534	6.9913057	30.1946354
H	5.2370998	7.7023744	28.5781453
H	4.6848203	3.7010517	30.8881504
H	2.9130286	3.8300344	31.1136748
H	3.9443938	5.2745513	31.3152381
H	1.4550201	2.3562811	27.8313567
H	1.8121579	2.5387637	29.5725613
H	2.9797186	1.7006157	28.5048558
H	3.5191880	3.0795571	25.3218041
H	2.6650435	4.5882369	24.8727411
H	1.7959705	3.2956491	25.7575026
H	-2.2996690	8.0661565	21.5602611
H	-3.0307700	6.4243198	21.5305466
H	-2.0766585	7.9504376	19.0494460
H	-2.5856013	6.2380223	18.8194922
H	0.0122180	11.0185821	19.5792005
H	1.5134275	12.0054793	19.7166759
H	0.8570193	11.8316372	22.3858273
H	-0.4591624	10.6709293	21.9964505
H	-4.2582813	8.1889194	22.5603296
H	-6.1672065	9.1750894	23.7880931
H	-6.2069018	9.1682841	26.2968332
H	-4.2794856	8.1718414	27.5667373
H	-2.3389893	7.2083696	26.3490523
H	-4.0890630	5.1368536	24.1372715
H	-4.3272642	2.6915543	24.5711435
H	-2.3011673	1.2122035	24.5976796
H	-0.0307619	2.1959173	24.1858186

H	0.2173959	4.6580119	23.7763778
H	-2.8116720	4.3272676	20.3926026
H	-2.5703854	1.8565609	20.3895068
H	-0.2968373	0.8064636	20.5281777
H	1.7450061	2.2594952	20.6759425
H	1.5114586	4.7541364	20.6846235
H	-2.5470698	4.8793727	16.3466861
H	-2.2514350	2.5065369	15.6384928
H	0.0069083	1.4228874	15.7716231
H	1.9672540	2.7188728	16.6509327
H	1.6707000	5.0913403	17.4018366
H	-3.1377544	8.6270384	17.3763148
H	-4.4415200	9.5734892	15.4963844
H	-3.7748075	9.1068328	13.1223931
H	-1.7621097	7.6751523	12.6563634
H	-0.4424897	6.7176222	14.5343226
H	0.1260013	12.9296518	18.0262793
H	-1.1519856	14.1542186	16.2850660
H	-1.4083583	13.1868979	13.9851123
H	-0.3898083	10.9540203	13.4511211
H	0.8666031	9.6990192	15.2030459
H	2.8100608	12.8660345	17.0438168
H	5.1694809	13.5461306	16.6148819
H	7.0321592	11.8902567	16.9008644
H	6.5191247	9.5457326	17.6347353
H	4.1543610	8.8575825	18.0843071
H	2.9967711	12.5132797	21.5639898
H	5.3853807	13.0634681	21.9500932
H	7.1167427	11.2485188	21.9648307
H	6.4294476	8.8621823	21.5943128
H	4.0203525	8.2961477	21.2075019
H	1.3251473	12.6374557	25.4170682
H	3.4797945	13.4948969	26.3364239
H	5.5457175	12.0746912	26.2423941
H	5.4406432	9.7834349	25.2253045
H	3.2703384	8.9027921	24.3321981
H	-0.4981245	9.8298869	26.7339278
H	-2.1973369	11.1162832	28.0141615
H	-3.4156447	13.0320693	26.9354165
H	-2.8998927	13.6483718	24.5581992
H	-1.1857446	12.4001784	23.2821041

Table 10. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^2\text{:}\eta^5\text{-}P_5)FeCp^*\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
Cu	-1.7931841	7.9201070	32.1071069
Cu	-1.8822969	8.3837193	35.7558931
Cu	-1.2543327	9.0764322	38.2979081
P	-1.3872966	11.3392863	38.2153664
P	0.6237264	7.8645088	38.7073787
P	-2.1695771	10.5917355	35.2936130
P	0.0194703	7.1396071	35.7493888
P	0.2818295	6.9332639	32.5427484
P	-1.8514382	10.3093074	32.0487306
Cl	-3.1565829	7.3619469	33.9939337



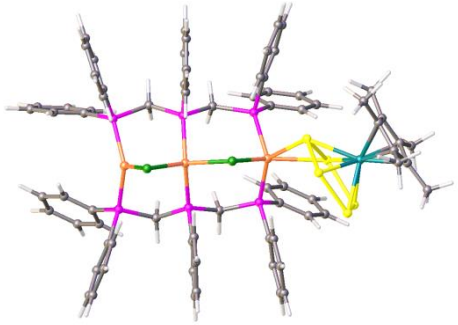
Cl	-3.1597308	7.8733224	37.7975282
Fe	-3.8275153	6.1293702	28.6979081
P	-4.7986333	5.4956912	30.7860331
P	-3.8848558	7.4464419	30.6700534
P	-1.9305861	7.1888331	29.6863878
P	-1.7427591	5.1038776	29.1399017
P	-3.4867438	4.0644590	29.8561575
C	-5.5451062	6.9341153	27.7876923
C	-5.4042967	5.5366073	27.4430107
C	-4.3645099	7.6288037	27.3260263
C	-6.7462292	7.5682194	28.4220965
C	-4.1376070	5.3687293	26.7656228
C	-6.4330979	4.4684757	27.6592207
C	-3.4938588	6.6618606	26.6951288
C	-4.1289475	9.1068790	27.4038490
H	-7.4652753	7.8962563	27.6402400
H	-6.4724431	8.4581637	29.0214589
H	-7.2770475	6.8635721	29.0909625
C	-3.6296720	4.0960629	26.1581683
H	-7.1196054	4.4145071	26.7865399
H	-7.0479400	4.6657155	28.5584980
H	-5.9698115	3.4706011	27.7830223
C	-2.2015213	6.9657323	25.9988412
H	-3.0493686	9.3489958	27.4391934
H	-4.6009803	9.5538816	28.3000937
H	-4.5577442	9.6112995	26.5106707
H	-3.9722592	3.2066821	26.7216432
H	-2.5233936	4.0671919	26.1280540
H	-3.9979759	3.9947257	25.1141588
H	-2.3888868	7.2328685	24.9360842
H	-1.5156072	6.0968754	26.0103859
H	-1.6726046	7.8167471	26.4701901
C	1.0741974	7.3038216	34.2060482
C	0.2924683	5.0882437	32.5014812
C	1.6550820	7.3975172	31.3859221
C	-1.4860636	11.2163174	33.6619896
C	-0.6335671	11.1660690	30.9403629
C	-3.4875321	11.0149553	31.5429021
H	2.0090683	6.7092638	34.2939553
H	1.3556688	8.3775037	34.1893671
C	1.4820498	4.3450851	32.3307889
C	-0.9333316	4.4126533	32.6717575
C	1.7299992	6.7578400	30.1255155
C	2.5779680	8.4274313	31.6729469
H	-0.3823003	11.1551613	33.7724736
H	-1.7515063	12.2876142	33.5421396
C	-0.0514543	10.4211839	29.8923597
C	-0.2695090	12.5251729	31.0907295
C	-4.6485007	10.4438502	32.1122567
C	-3.6226872	12.0516544	30.5946101
C	1.3465132	7.5701695	37.0089715
C	-0.2356728	5.3327792	36.0040356
H	2.4442005	4.8607864	32.1870550
C	1.4403593	2.9426113	32.3230390
C	-0.9662907	3.0080534	32.6760845
H	-1.8610035	4.9908936	32.8045790
H	1.0260617	5.9500513	29.8741948

C	2.7113318	7.1274497	29.1925413
C	3.5601165	8.7942490	30.7376006
H	2.5464827	8.9598994	32.6347089
C	-1.2824608	11.8158490	36.4093186
C	-3.9164943	11.1875659	35.3375485
H	-0.3172861	9.3604496	29.7669041
C	0.8600959	11.0218282	29.0078596
C	0.6477532	13.1212146	30.2104391
H	-0.7067558	13.1386834	31.8926107
H	-4.5574856	9.6096508	32.8249159
C	-5.9182553	10.9318048	31.7668559
C	-4.8981346	12.5267002	30.2424869
H	-2.7326073	12.4907841	30.1208409
H	1.7628506	8.5450725	36.6785320
H	2.1706356	6.8256871	37.0275195
C	-1.5540716	4.8840601	36.2280910
C	0.8278727	4.4044365	36.0163868
H	2.3689470	2.3693728	32.1777891
C	0.2159018	2.2728656	32.4958703
H	-1.9267564	2.4887220	32.8103852
H	2.7586396	6.6076984	28.2233593
C	3.6329710	8.1442512	29.4955481
H	4.2745196	9.5936116	30.9865788
H	-1.6255035	12.8566754	36.2309885
H	-0.2054931	11.7512347	36.1450919
C	-4.2666148	12.5317859	35.0843973
C	-4.9268022	10.2557293	35.6552650
H	1.3027868	10.4227868	28.1980978
C	1.2127603	12.3714965	29.1643761
H	0.9184872	14.1803477	30.3403551
H	-6.8124505	10.4858693	32.2275145
C	-6.0468866	11.9734499	30.8318638
H	-4.9907975	13.3358518	29.5017000
C	0.4532309	6.1954957	39.4757065
C	2.0277556	8.5939869	39.6665619
H	-2.3828089	5.6073314	36.2192158
C	-1.8020208	3.5220240	36.4659573
C	0.5744345	3.0456156	36.2528573
H	1.8651316	4.7315180	35.8399842
H	0.1848984	1.1725530	32.4862486
H	4.4077992	8.4264905	28.7666968
C	-0.0511610	12.3481181	38.9929335
C	-2.9370060	12.1209032	38.8495789
H	-3.4964164	13.2787635	34.8324401
C	-5.6074494	12.9380549	35.1474481
C	-6.2690194	10.6670441	35.7170296
H	-4.6555907	9.2088767	35.8575328
H	1.9297668	12.8412441	28.4737783
H	-7.0441151	12.3505845	30.5575387
C	-0.8430292	5.6993268	39.7263999
C	1.5809670	5.4260073	39.8417792
C	3.1422423	9.2214070	39.0711795
C	1.9353488	8.5702420	41.0786229
H	-2.8334468	3.1813275	36.6429812
C	-0.7413353	2.6034108	36.4801521
H	1.4082473	2.3274639	36.2608805
C	0.3767105	11.9571320	40.2812074

C	0.5366172	13.4830517	38.3920133
C	-3.0165108	13.4981577	39.1521334
C	-4.0599566	11.2923033	39.0612742
H	-5.8709430	13.9878688	34.9483318
C	-6.6109426	12.0050533	35.4644939
H	-7.0499628	9.9332704	35.9685709
H	-1.7223486	6.2927123	39.4282435
C	-1.0068858	4.4456479	40.3408587
C	1.4095024	4.1748451	40.4517774
H	2.5975534	5.8118742	39.6666441
H	3.2482869	9.2608234	37.9768988
C	4.1463187	9.8001538	39.8670700
C	2.9402762	9.1456376	41.8699891
H	1.0769557	8.0808907	41.5656771
H	-0.9365906	1.5365865	36.6689323
H	-0.0578167	11.0607123	40.7512625
C	1.3561195	12.6956554	40.9617041
C	1.5262334	14.2144864	39.0715445
H	0.2247395	13.8130378	37.3896711
H	-2.1386440	14.1487483	39.0172394
C	-4.2117681	14.0403970	39.6488422
C	-5.2532983	11.8432472	39.5576018
H	-3.9970653	10.2156712	38.8340412
H	-7.6626241	12.3262853	35.5163138
H	-2.0209315	4.0656033	40.5369038
C	0.1151050	3.6849026	40.7050306
H	2.2909905	3.5810309	40.7384261
H	5.0127064	10.2780762	39.3849027
C	4.0508854	9.7622131	41.2666510
H	2.8578761	9.1055856	42.9670144
H	1.6769336	12.3794411	41.9653795
C	1.9335404	13.8260403	40.3580396
H	1.9761000	15.0977358	38.5926772
H	-4.2662251	15.1135877	39.8878643
C	-5.3312863	13.2140651	39.8519556
H	-6.1247243	11.1913465	39.7214017
H	-0.0161396	2.7063585	41.1918704
H	4.8421683	10.2084633	41.8877649
H	2.7051033	14.4030509	40.8900217
H	-6.2648555	13.6410498	40.2493480

Table 11. Cartesian coordinates of the optimized geometry of $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2\{(\mu_3,\eta^2\text{:}\eta^5\text{-}As_5)FeCp^*\}]^+$ at the BP86/def2-SVP level of theory.

Atom	x	y	z
As	2.3862544	5.5462275	25.0796838
As	1.5642472	3.4616984	25.8669656
As	0.4529523	3.8297392	27.9150719
As	0.6579424	6.1115210	28.4702934
As	1.8952460	7.1956703	26.7659443
Cu	0.7026524	7.4638325	24.3795085
Cu	-1.9389174	9.9621332	23.7274559
Cu	-3.6465629	11.6931208	22.5368730
Fe	2.7137709	4.9383701	27.5397865
Cl	-0.8969226	8.7984420	25.5527991
Cl	-3.6989115	11.2900943	24.8086220



P	2.0957019	9.0979228	23.2868157
P	-0.2581321	11.3447659	23.0852987
P	-2.2658129	13.3558562	21.8368704
P	-4.8488761	10.3224513	21.1875477
P	-2.9162282	8.2863923	22.5382649
P	-0.5392730	6.1461147	22.9051780
C	4.7490060	5.4730135	27.6760822
C	4.0924460	5.6993959	28.9436033
C	3.5595932	4.4356459	29.4022004
C	3.8896593	3.4284718	28.4188319
C	4.6229707	4.0702136	27.3502890
C	5.5377484	6.4880235	26.9041205
C	4.0868248	6.9873737	29.7118366
C	2.9020355	4.1863595	30.7263353
C	3.6332351	1.9570446	28.5514563
C	5.2616853	3.3789135	26.1825771
C	1.2336545	10.4826434	22.3467337
C	-0.6041969	12.5170686	21.6562870
C	-3.8275180	8.7704842	20.9698006
C	-1.7601398	7.0210988	21.7721286
C	3.2626171	8.4913447	21.9723616
C	3.3964651	9.0747834	20.6922481
C	4.3105469	8.5556480	19.7581401
C	5.1101657	7.4503827	20.0876088
C	4.9862487	6.8621377	21.3577904
C	4.0688779	7.3733780	22.2874301
C	3.2207060	10.0376452	24.4211139
C	4.5403045	10.3928914	24.0660390
C	5.3480489	11.1029515	24.9702008
C	4.8468317	11.4655967	26.2320306
C	3.5334470	11.1164024	26.5889853
C	2.7239580	10.3992941	25.6933100
C	0.4109372	12.4687821	24.3847647
C	1.4860091	13.3526945	24.1480065
C	1.9377458	14.2036889	25.1669384
C	1.3190419	14.1795102	26.4298670
C	0.2493930	13.3026948	26.6703070
C	-0.2070969	12.4481607	25.6526102
C	-1.9841251	14.7980281	22.9529648
C	-1.2016867	15.9060938	22.5559264
C	-1.0407732	16.9982098	23.4209072
C	-1.6621762	16.9959176	24.6832915
C	-2.4384112	15.8963417	25.0814659
C	-2.6009624	14.7963606	24.2214044
C	-2.5263433	14.1760840	20.1987490
C	-1.8782936	13.7764429	19.0109529
C	-2.1676595	14.4112244	17.7904418
C	-3.1083806	15.4512866	17.7383139
C	-3.7654522	15.8521001	18.9152225
C	-3.4812099	15.2186335	20.1338781
C	-5.1911934	10.8467595	19.4513138
C	-5.0773468	9.9955572	18.3300767
C	-5.3909473	10.4687843	17.0441181
C	-5.8276071	11.7913589	16.8650456
C	-5.9402546	12.6459347	17.9752432
C	-5.6166077	12.1798658	19.2581249
C	-6.4967770	9.7529210	21.7986760

C	-7.4650288	9.1876258	20.9398778
C	-8.7078077	8.7839836	21.4518418
C	-8.9944064	8.9453867	22.8189856
C	-8.0357402	9.5127474	23.6740210
C	-6.7900529	9.9216044	23.1691236
C	-4.1773262	7.3230746	23.4773597
C	-4.9477938	6.2949742	22.8919770
C	-5.9288826	5.6327147	23.6441462
C	-6.1485653	5.9905108	24.9865174
C	-5.3804054	7.0066613	25.5754185
C	-4.3966298	7.6731855	24.8262696
C	-1.6114223	4.8590306	23.6768580
C	-2.1585066	3.7876917	22.9344758
C	-2.9989082	2.8543737	23.5594848
C	-3.3117422	2.9907920	24.9240621
C	-2.7805632	4.0603188	25.6614363
C	-1.9254645	4.9893246	25.0445727
C	0.4826815	5.2195115	21.6670486
C	0.9313053	3.9082765	21.9486159
C	1.7866014	3.2383082	21.0585446
C	2.2131272	3.8642607	19.8762434
C	1.7872081	5.1725994	19.5943328
C	0.9359693	5.8462463	20.4844399
H	5.1189729	7.5076620	27.0095787
H	5.5691246	6.2495383	25.8234765
H	6.5873009	6.5165814	27.2705128
H	4.9857611	7.0485044	30.3635716
H	3.1953626	7.0753445	30.3627003
H	4.1003711	7.8679689	29.0404748
H	3.6671925	3.9308785	31.4916321
H	2.1836353	3.3451281	30.6782083
H	2.3505514	5.0758965	31.0876000
H	3.5381251	1.4633463	27.5649794
H	2.7058145	1.7494531	29.1197448
H	4.4737204	1.4692703	29.0918856
H	6.2962794	3.0633844	26.4405369
H	5.3249075	4.0405659	25.2967135
H	4.7004170	2.4727164	25.8828175
H	0.8389465	10.0098234	21.4223089
H	1.9969106	11.2317372	22.0461982
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H	0.2186648	13.2454941	21.4941647
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H	-2.3309731	6.2553367	21.2040989
H	-1.1595719	7.6015581	21.0413944
H	2.7993679	9.9513859	20.4046491
H	4.4013069	9.0284193	18.7680167
H	5.8281870	7.0482161	19.3568524
H	5.6032893	5.9915247	21.6269032
H	3.9738966	6.8884296	23.2718999
H	4.9448858	10.1094437	23.0829210
H	6.3769193	11.3718358	24.6853095
H	5.4827692	12.0203603	26.9389842
H	3.1323717	11.3987634	27.5738527
H	1.6961260	10.1262786	25.9774878
H	1.9857637	13.3845381	23.1663929

H	2.7771991	14.8889846	24.9751071
H	1.6733639	14.8505292	27.2274529
H	-0.2401422	13.2825304	27.6559064
H	-1.0476035	11.7619648	25.8353752
H	-0.7306428	15.9255416	21.5605187
H	-0.4332990	17.8604711	23.1058080
H	-1.5414739	17.8587523	25.3561845
H	-2.9259610	15.8908841	26.0681083
H	-3.1982096	13.9257049	24.5370781
H	-1.1315107	12.9687041	19.0215492
H	-1.6462529	14.0912927	16.8753967
H	-3.3274564	15.9522077	16.7832692
H	-4.5016401	16.6700517	18.8867493
H	-3.9959271	15.5509133	21.0492841
H	-4.7487217	8.9520083	18.4479171
H	-5.2989424	9.7951475	16.1783315
H	-6.0773131	12.1581196	15.8578678
H	-6.2727477	13.6860689	17.8416129
H	-5.6877189	12.8596325	20.1219039
H	-7.2576212	9.0765953	19.8643801
H	-9.4607269	8.3490198	20.7767386
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H	-1.5018625	5.8247142	25.6237054
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H	2.8773538	3.3348547	19.1764704
H	2.1212533	5.6779162	18.6756989
H	0.6335627	6.8766868	20.2434137

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