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Embryonic Brass: Pseudo Two Electron Cu/Zn Clusters

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Materials and Methods

Spectroscopy NMR spectra were recorded on a Bruker Avance III AV400US (^{1}H, 400 MHz), a Bruker DRX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) and a Bruker Avance II AV500 with a cryo probe (^{13}C, 125 MHz). The deuterated solvents (CD_2Cl_2, C_6D_6) were degassed by freeze-pump-thaw method and stored over molecular sieves. Chemical shifts are given relative to TMS and were referenced to the residual solvent peak as internal standards. Chemical shifts are reported in parts per million, downfield shifted from TMS, and are consecutively reported as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, q = quartet and m = multiplet), coupling constant (J in Hz) and assignment. IR spectra were recorded on a Bruker Alpha-P Fourier transform spectrometer. FT-IR spectra were measured in an ATR setup with a Bruker Alpha FTIR spectrometer under an inert gas atmosphere in a glove-box.

Elemental Analysis (EA) and Atomic Absorption Spectroscopy (AAS) EA and AAS measurements for compound **2**[BAr_4^F] were conducted in the Microanalytical Laboratory Kolbe in Mülheim an der Ruhr.

Spectrometry Mass spectrometry for compound **1** was conducted with an Exactive™ Plus Orbitrap system from the Thermo Scientific company; Ionisation method: liquid injection field desorption ionization (LIFDI; special ionization cell obtained from Linden CMS GmbH, Leeste, Germany; http://www.linden-cms.de), solvent: toluene. The sample is applied on a tungsten wire which is coated with thousands of micro graphite dendrites. By applying a potential between the emitter and the counter electrode of 10 kv the sample molecules are ionised and subsequently accelerated to the counter electrode and eventually to the detector. The resulting ions are radical cations, e.g. $[M]^{\bullet+}$.

X-Ray crystallography The X-ray diffraction reflections for **1** and **2**[BAr_4^F] · 5 C_6H_5F were collected on a Bruker diffractometer equipped with a IμS microfocus source and a CMOS detector (APEX III, κ-CMOS) using Mo-Kα irradiation (λ = 0.71073 Å) from a Helios optic. The crystals were coated with a perfluoropolyether, picked up with a Mitegen microsampler, and immediately mounted in the nitrogen cold gas stream (100 K) of the diffractometer. Data collection and reduction were conducted with the software APEX III of the Bruker company.[1] Absorption corrections were performed using SADABS in APEX III. The crystal structures were solved by intrinsic phasing using SHELXT and refined with SHELXL-2014.[2] Standard similar distance restraints and constraints on atomic displacement parameters (ADPs) were used to model disordered regions. Anisotropic ADPs were introduced for all non-hydrogen atoms. Hydrogen atoms were placed at geometrically calculated positions and refined with the appropriate riding model. Disordered fluorobenzene solvent molecules in **2**[BAr_4^F] · 5 C_6H_5F were visible in the difference Fourier maps but could not be modelled reasonably and were therefore removed with the PLATON/SQUEEZE procedure.[3] CCDC 1854851-1854852 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Remark: We also tested the refinement of the crystal structures of **1** and **2**[BAr_4^F] with different alternative models involving the exchange of Cu and Zn in the equatorial and the apical

positions of the respective trigonal bipyramids. As a result we obtained lower reliability factors R_1, wR_2 and GOF (goodness of fit) values in both cases, compared to the presented models in this publication.

Table S1 Crystallographic data and refinement details for **1** and **2**[BAr_4^F] · 5 C_6H_5F.

	1	**2**[BAr_4^F] · 5 C_6H_5F
Empirical formula	$C_{50}H_{75}Cu_3Zn_4$	$C_{112}H_{112}BCu_2F_{29}Zn_5$
M_r	1128.33	2473.89
T [K]	100	100
λ [Å]	0.71073	0.71073
Crystal size [mm^3]	0.192 x 0.132 x 0.120	0.206 x 0.111 x 0.051
Crystal system	Monoclinic	Monoclinic
Space group	*P n*	*C c*
a [Å]	16.1793(14)	23.729(3)
b [Å]	37.930(3)	22.495(3)
c [Å]	17.4798(15)	36.442(5)
α [°]	90	90
β [°]	105.636(3)	90.573(4)
γ [°]	90	90
V [$Å^3$]	10330.1(15)	19451(4)
Z	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.451	1.394
μ [mm^{-1}]	3.067	1.726
F (000)	4656	8264
θ range [°]	2.276 - 25.721	2.4679 – 24.894
Reflections collected / unique	347810 / 37771	104015 / 32525
R_{int}	0.0510	0.0665
Reflections observed [I > 2σ(I)]	34349	21607
Completeness to θ = 67.684° [%]	99.9	99.9
Data / restraints / Parameters	37771 / 2087 / 2248	32525 / 1364 / 2455
Goodness-of-fit on F^2	1.061	1.024
$R1$ [$I > 2\sigma(I)$]	0.0408	0.0663
wR2 (all data)	0.0993	0.1685
ΔF_{max}; ΔF_{min} [e $Å^{-3}$]	0.831; -0.874	1.736; -0.595

Experimental Section

All experiments were conducted using standard Schlenk and glovebox techniques under an atmosphere of purified argon. All solvents were dried and saturated with argon prior to their use. $[Zn_2Cp^*_2]$[4, 5] and $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$[6] were prepared according to literature procedures.

Synthesis of $[Cp^*Zn_2(THF)_3][BAr_4^F]$ i) A mixture of 100 mg (0.249 mmol) $[Zn_2Cp^*_2]$ and 262 mg (0.249 mmol) $[FeCp_2][BAr_4^F]$ were dissolved in THF (5 mL) at room temperature and stirred for 15 min, whereupon the initial blue solution immediately turned orange. The solvent was removed in vacuum and the residue was washed with n-hexane (3 x 4 mL). Recrystallization from a saturated THF solution of $[Cp^*Zn_2(THF)_3][BAr_4^F]$ at -30 °C gave suitable colourless crystals for single crystal X-ray diffraction.
Yield: 152 mg (113 mmol) of colourless crystals (45 %);
ii) A solution of 100 mg (0.074 mmol) $[Cp^*Zn_2(Et_2O)_3]$ in 3 mL THF was stirred for 15 min at room temperature. The solvent was removed in vacuum and the residue was washed with n-hexane (3 x 4 mL). Recrystallization of the crude product from a saturated THF solution at – 30 °C gave suitable colourless crystals for single crystal X-ray diffraction.
Yield: 80 mg (59 mmol) of colourless crystals (80 %).
Elemental and AAS analysis [%] calculated for $C_{54}H_{51}BF_{24}O_3Zn_2$: C, 48.20; B, 0.80; H, 3.82; F, 33,89; Zn, 9.72; Found: C, 48.16; B, 0.78; H, 3.93; F, 33,81; Zn, 9.69.
^{1}H NMR (298 K, 250.1 MHz, CD_2Cl_2): δ [ppm] = 2.00 (q, 12H, THF), 2.07 (s, 15H, Cp*), 3.85 (t, 12H, THF), 7.57 (s, 4H, $[BAr_4^F]^-$), 7.72 (s, 8H, $[BAr_4^F]^-$).
^{13}C NMR (298 K, 62.9 MHz, CD_2Cl_2): δH [ppm] = 10.33 (s, C_5Me_5), 25.62 (s, THF), 70.99 (s, THF), 109.24 (s, C_5Me_5), 117.90 (s, $[BAr_4^F]^-$), 125.08 (q, JC-F = 272.4 Hz, CF_3), 129.33 (q, JC-F = 31.5 Hz, $[BAr_4^F]^-$), 135.23 (s, $[BAr_4^F]^-$), 162.19 (q, JC-B = 51.5 Hz, $[BAr_4^F]^-$).
^{11}B NMR (298 K, 80.3 MHz, CD_2Cl_2): δ [ppm] = -6.59 (s, $[BAr_4^F]^-$).
IR (ATR, 298 K): ν [cm^{-1}] = 2876.19 (w), 1597.15 (w), 1450.46 (s), 1342.48 (s), 1266.29 (s), 1102.55 (s), 1011.83 (m), 943.72 (m), 917.42 (m), 878.93 (m), 830.71 (m), 737.66 (w), 708.65 (m), 676.40 (m), 663.75 (m), 575.31 (w), 506.26 (w), 443.37 (w).

Synthesis of $[Zn_2CuCp^*_3]$ A suspension of 600 mg (1.50 mmol) $[Zn_2Cp^*_2]$ and 183 mg (1.50 mmol) Cu(OAc) in benzene (5 mL) was stirred at room temperature for 2 days. The dark red suspension was filtered. The residue was extracted with warm benzene (2 x 3 mL). The volume

of the combined filtrates was reduced under vacuum for crystallization of the product at 8 °C overnight. Pale-yellow crystals were isolated by filtration and washed with *n*-hexane (3 x 2 mL). The volume of the filtrate was further reduced in vacuum to give another crop of yellow crystals at 8 °C overnight.

Yield: 340 mg of pale-yellow crystals (57 % based on Cp*).

^{1}H NMR (298 K, 400 MHz, C_6D_6): δ [ppm] = 2.07 (s, 30H, ZnC_5Me_5), 2.23 (s, 15H, CuC_5Me_5).

^{13}C NMR (298 K, 100 MHz, C_6D_6): δ [ppm] = 10.90 (ZnC_5Me_5), 12.17 (CuC_5Me_5), 104.62 (CuC_5Me_5), 110.18 (ZnC_5Me_5).

IR (ATR 298 K): $\tilde{\nu}$ [cm^{-1}] = 2970 (m), 2901 (s), 2856 (s), 2722 (w), 1476 (m), 1419 (s), 1375 (s), 1159 (m), 1020 (w), 976 (m), 794 (m), 616 (w), 588 (m).

Synthesis of $[Zn_4Cu_3](Cp^*)_5$ (**1**) The solvent of the filtrate from the second crop of the synthesis of **$[Zn_2CuCp^*_3]$** is removed in vacuum. The residue is dissolved in a minimum amount of THF. Crystallization at -30 °C afforded red single crystals of **2**, which were individually isolated and separated from single crystals of **$[Zn_2CuCp^*_3]$** by crystal picking.

^{1}H NMR (298 K, 400 MHz, C_6D_6): δ [ppm] = 2.08 (s, 45H, CuC_5Me_5), 2.19 (s, 30H, $ZnZnC_5Me_5$).

^{13}C NMR (298 K, 125 MHz, C_6D_6): δ [ppm] = 10.48 ($CuC_5\mathit{Me}_5$), 11.38 ($ZnZnC_5\mathit{Me}_5$), 105.32 ($Cu\mathit{C}_5Me_5$), 108.18 ($ZnZn\mathit{C}_5Me_5$).

LIFDI-MS: m/z [a.u.] 1128 ([M]$^+$), 927 ([M-ZnCp*]$^+$), 861 ([M-ZnZnCp*]$^+$).

Synthesis of $\{[Zn_5Cu_2](Cp^*)_5\}[BAr^F_4]$ (**2**[BAr^F_4]) A mixture of 80 mg (0.133 mmol) **$[Zn_2CuCp^*_3]$** and 360 mg (0.266 mmol) [$Cp^*Zn_2(Et_2O)_3$][BAr^F_4] was dissolved in fluorobenzene (3 mL). The red solution was stirred for 1.5 h at room temperature and subsequently filtered. The filtrate was concentrated and stored at -30 °C for a week giving dark red crystals as **2**[BAr^F_4] · 5 C_6H_5F covered by a sticky red residue. The crystals were isolated by filtration and recrystallized from fluorobenzene at -30 °C. After two recrystallization steps, **2**[BAr^F_4] was isolated as an analytically pure sample.

Yield: 30 mg (0.015 mmol) of dark red crystals (23 % based on Cu).

Elemental and AAS analysis [%] calculated for $H_{87}BC_{82}F_{24}Cu_2Zn_5$: H 4.40, B 0.54, C 49.41, F 22.87, Cu 6.38, Zn 16.40; found: H 4.62, B 0.47, C 51.48, F 20.20, Cu 6.48, Zn 15.98.

^{1}H NMR (298 K, 400 MHz, CD_2Cl_2): δ [ppm] = 1.96 (s, 30H, $ZnZnC_5Me_5$), 2.04 (s, 15H, ZnC_5Me_5), 2.12 (s, 30 H, CuC_5Me_5), 7.56 (s, 4H, $[BAr_4^F]^-$), 7.72 ppm (s, 8H, $[BAr_4^F]^-$).

IR (ATR 298 K): $\tilde{\nu}$ [cm^{-1}] = 2905(w), 2860 (w), 1610 (w), 1454 (w), 1416 (w), 1380 (w), 1272 (w), 1272 (m), 1154 (s), 1116 (m), 1022 (s), 934 (w), 886 (w), 838 (m), 794 (m), 714 (m), 681 (m), 669 (m).

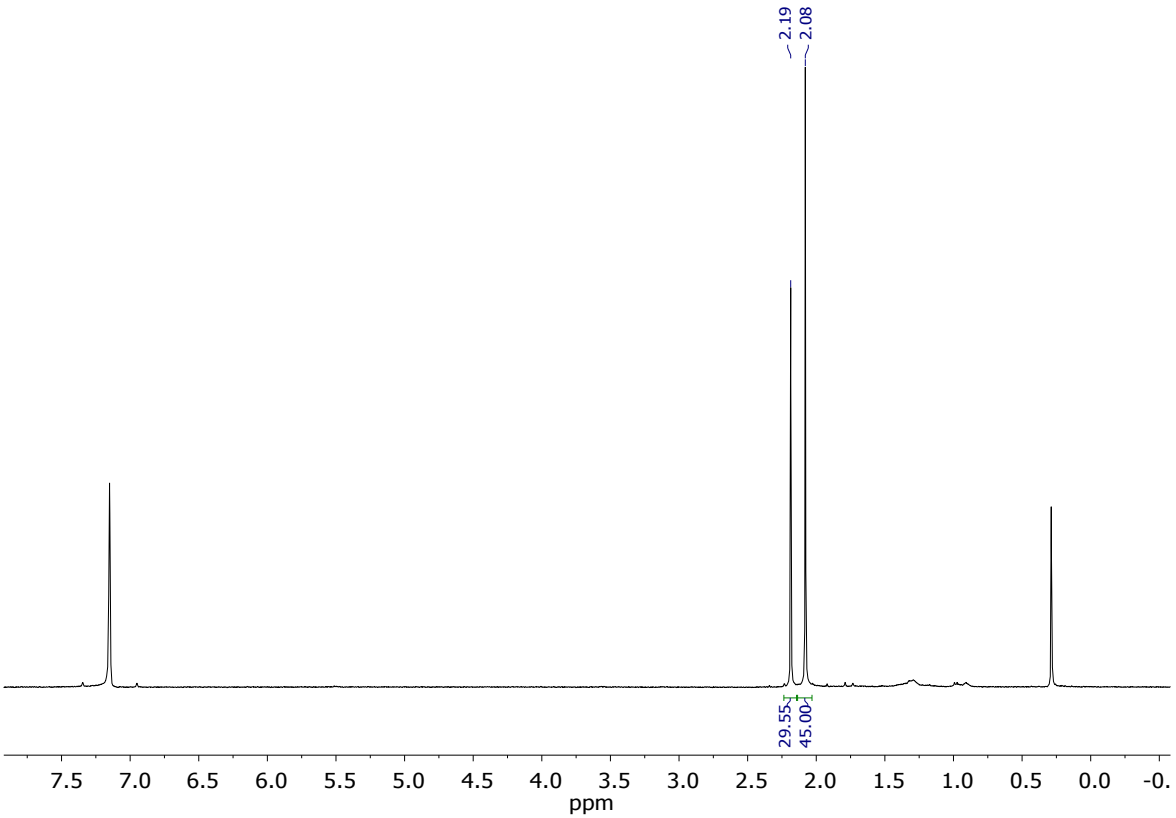


Figure S1 ^{1}H NMR spectrum of **1** recorded at room temperature in C_6D_6.

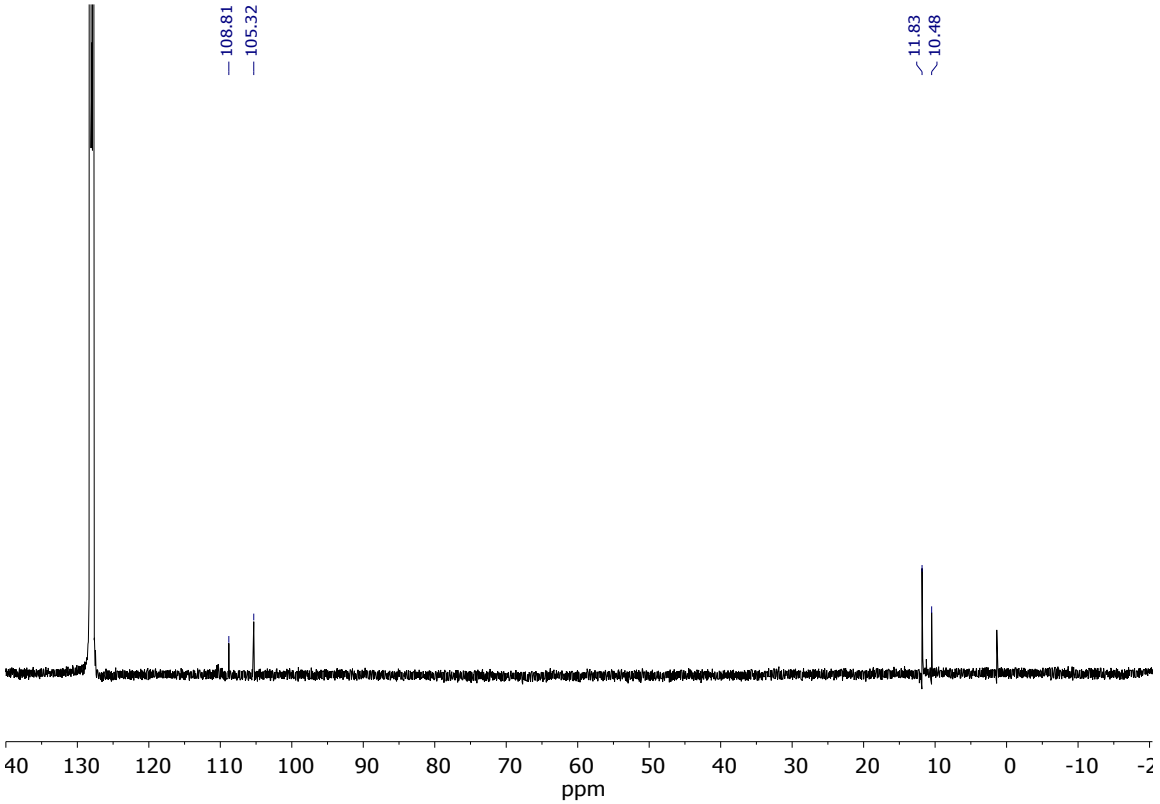


Figure S2 ^{13}C NMR spectrum of **1** recorded at room temperature in C_6D_6.

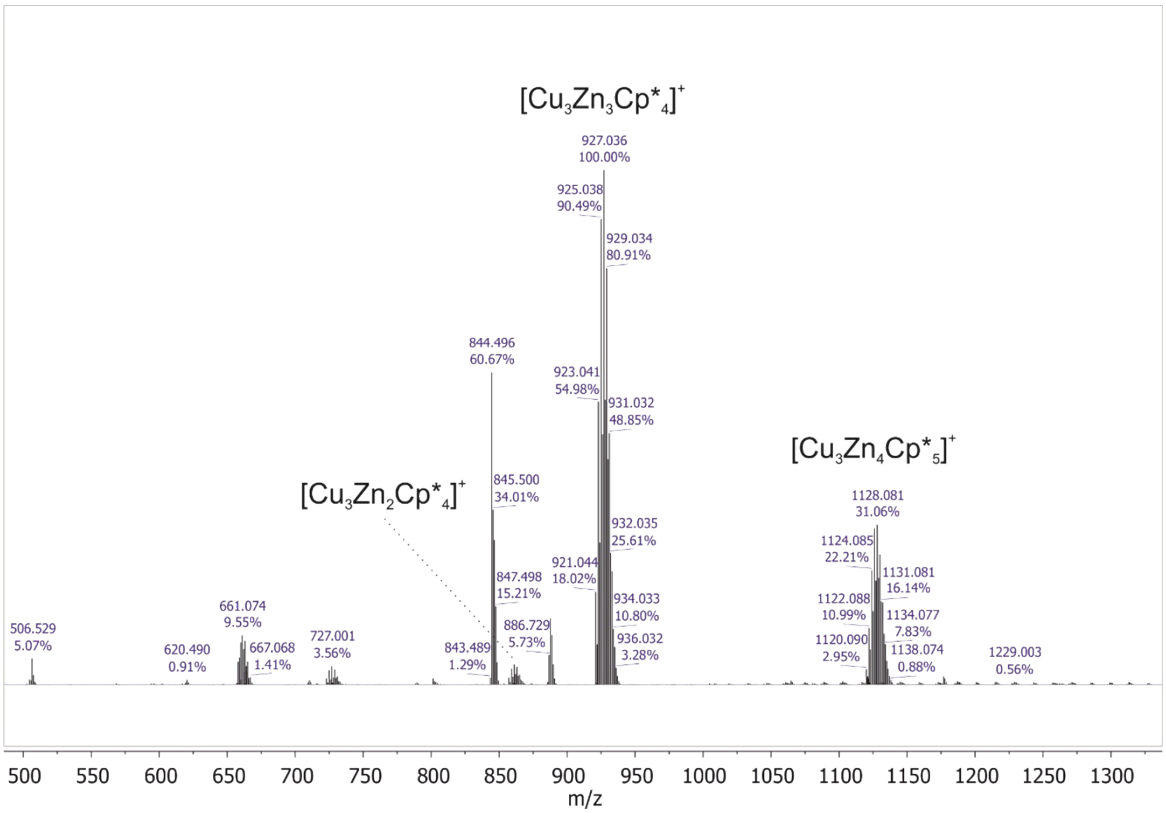


Figure S3: LIFDI-MS spectrum of **1**, m/z = 1128 $[M]^+$, 927 $[M\text{-}ZnCp^*]^+$, 861 $[M\text{-}ZnZnCp^*]^+$.

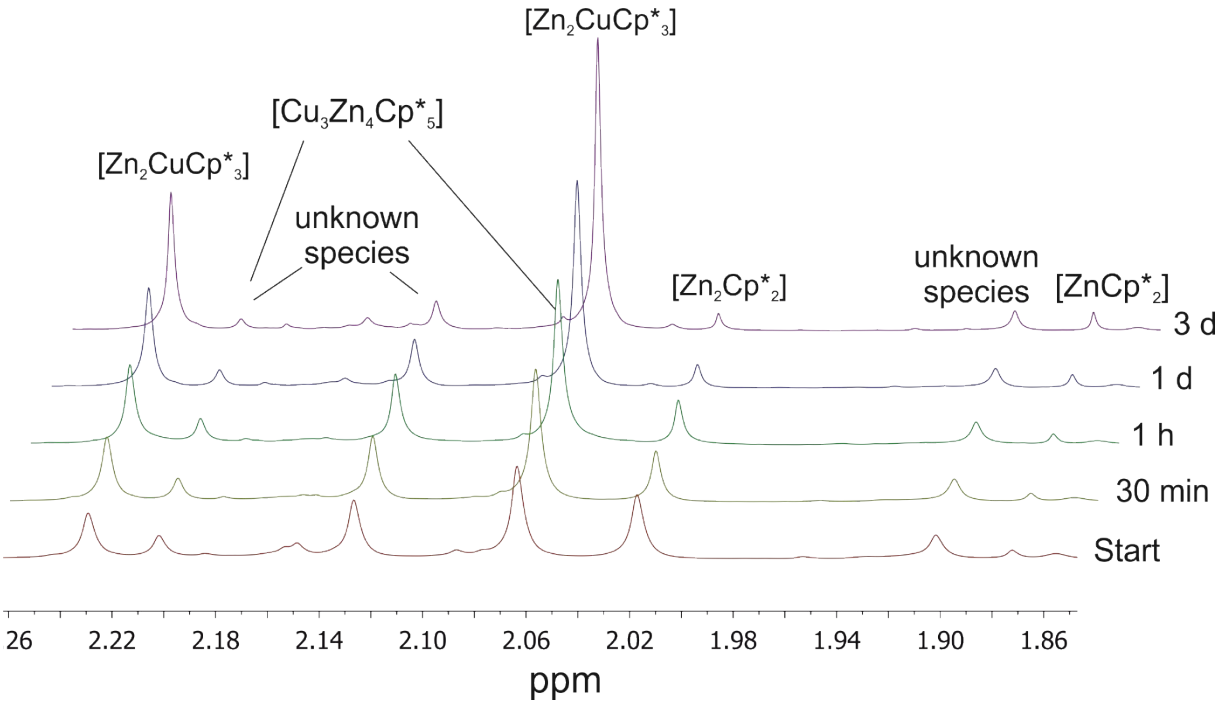
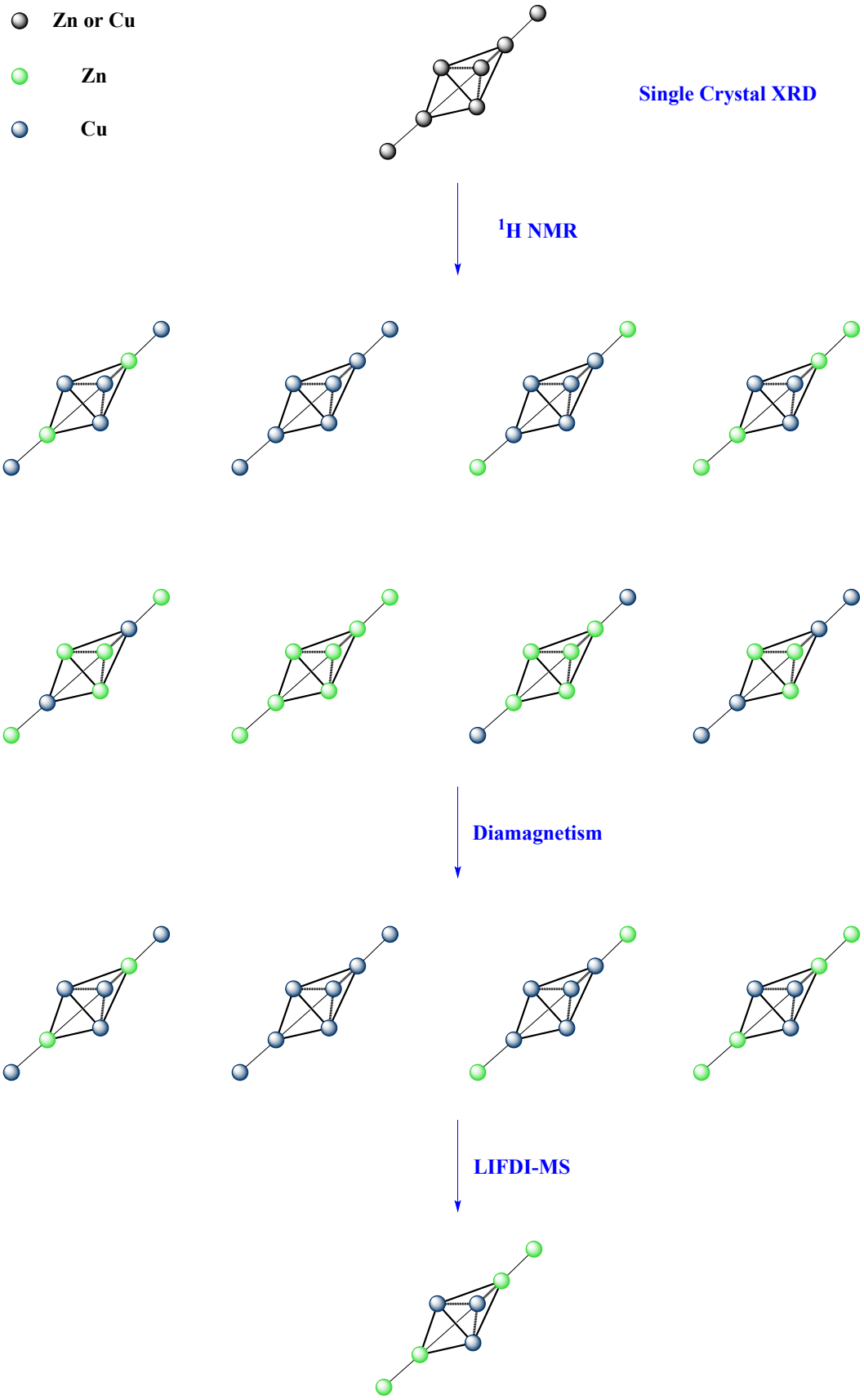


Figure S4 ^1H NMR spectra of a 1:1 mixture of Cu(OAc) and $[Zn_2Cp^*_2]$ in C_6D_6 at room temperature over a period of 3 days.



Scheme S1 Systematic determination of the composition and the assignment of Zn/Cu to the correct position in the molecular structure of **1**. The Cp* rings in the isomer models are omitted for clarity.

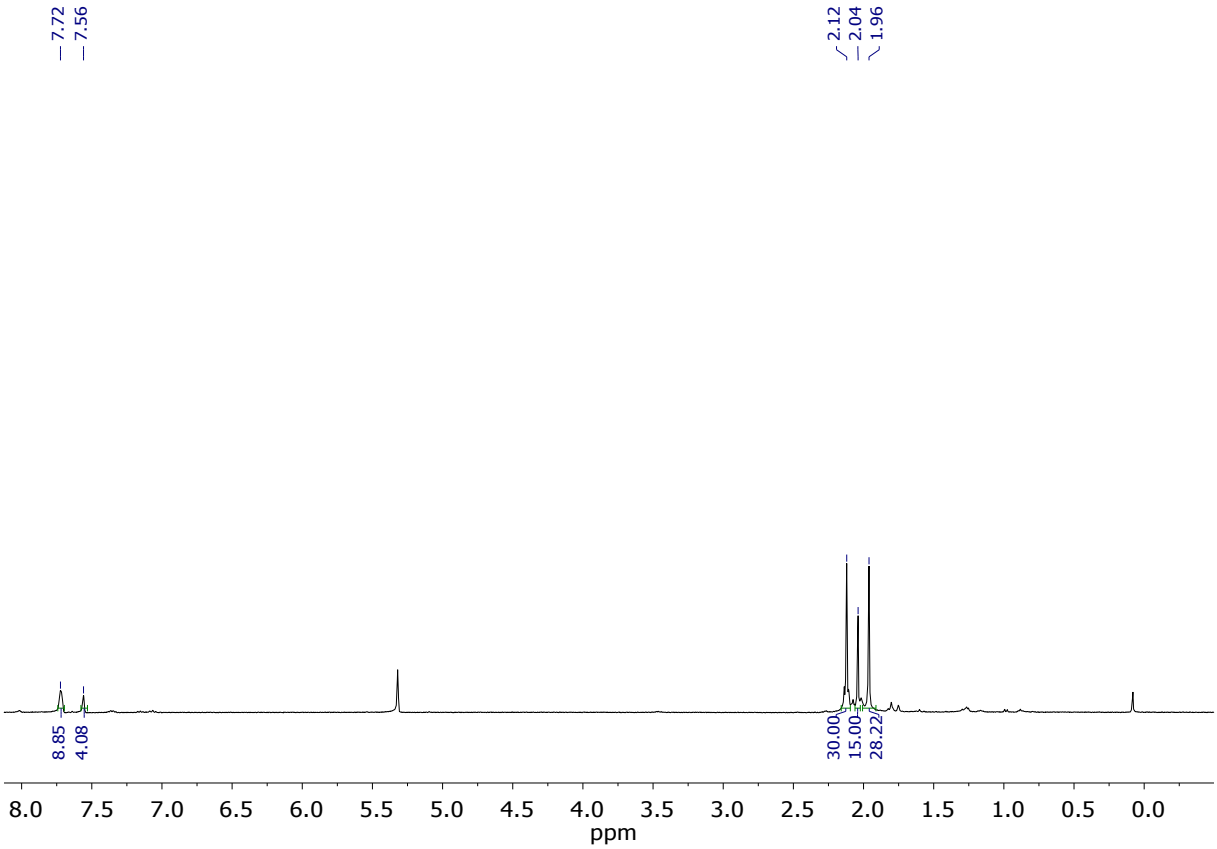


Figure S5 ^{1}H NMR spectrum of **2**[BAr_4^F] recorded at room temperature in CD_2Cl_2.

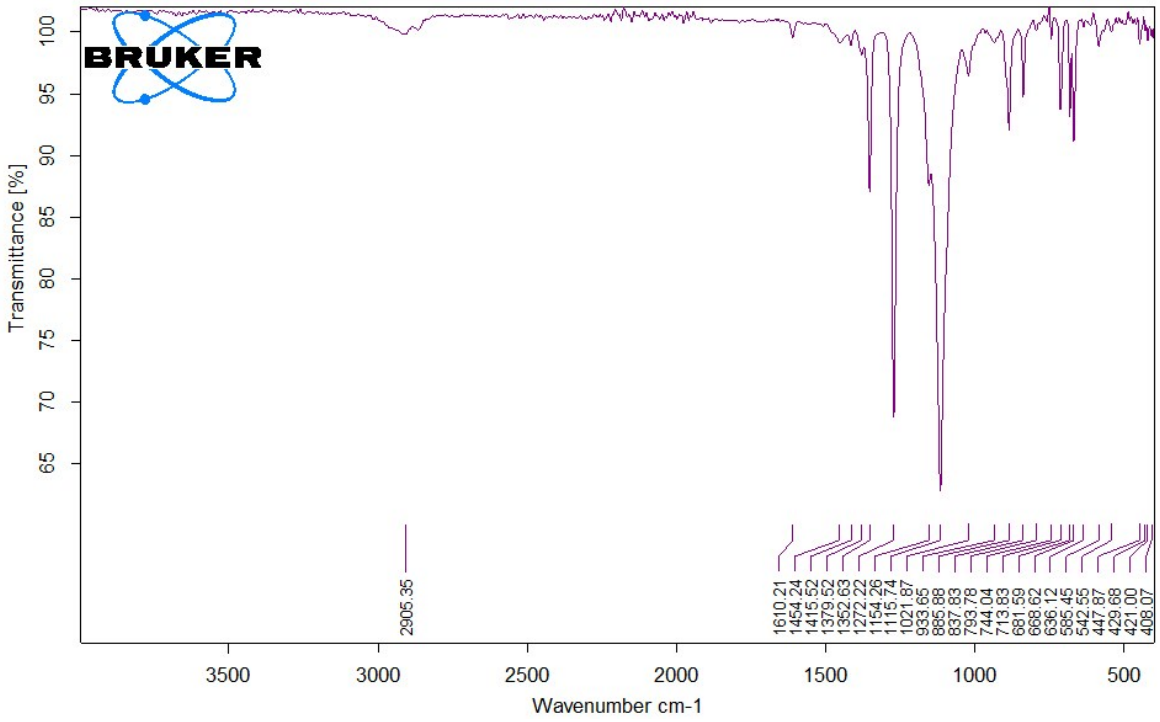


Figure S6 IR spectrum of **2**[BAr_4^F].

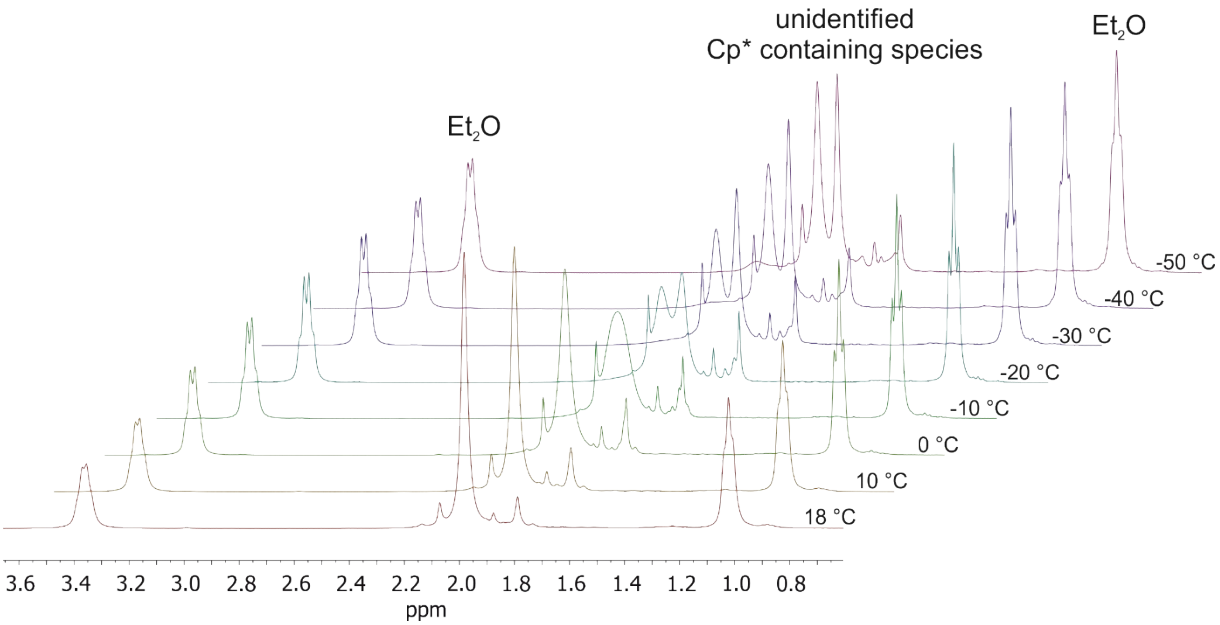
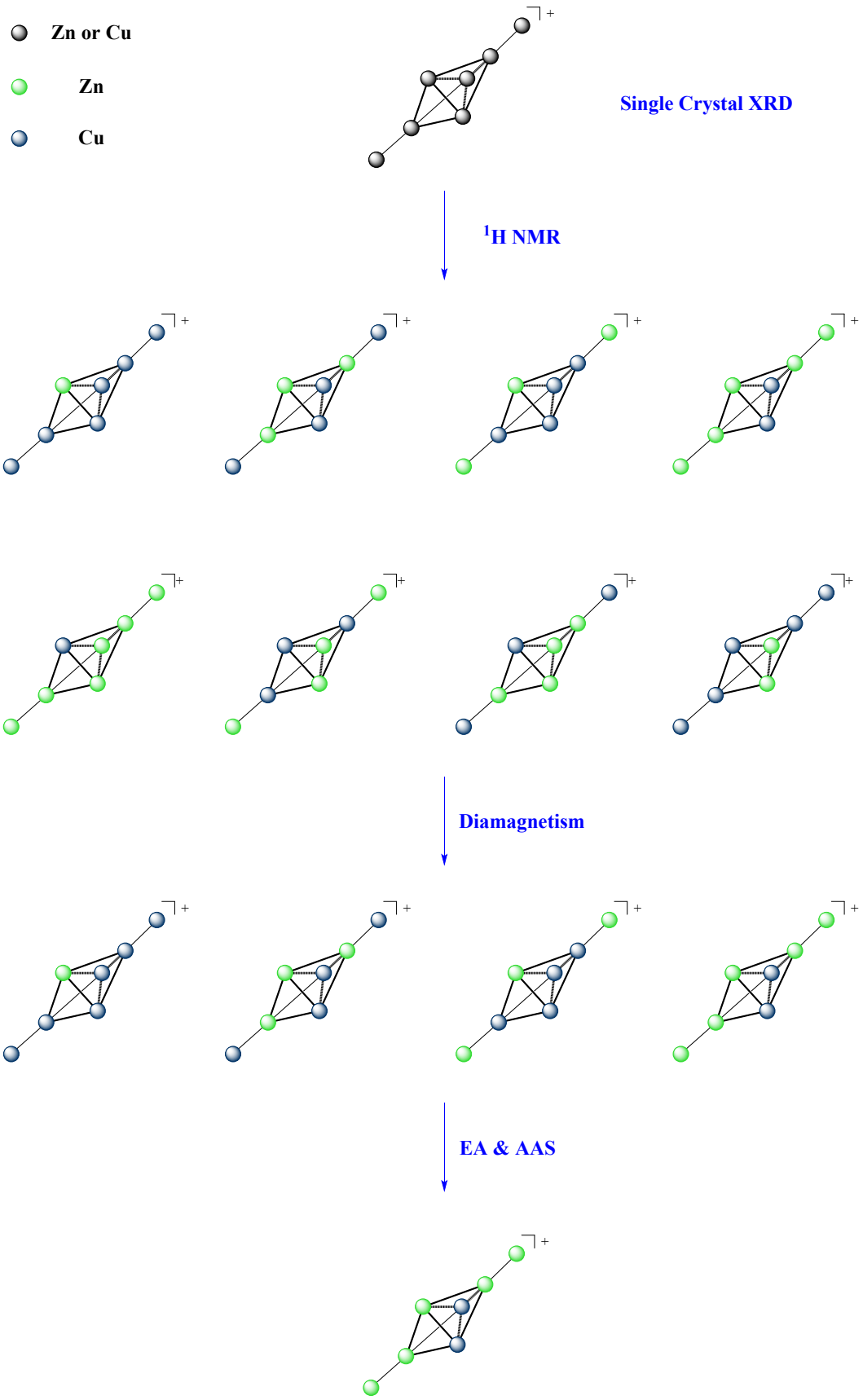


Figure S7 ^{1}H NMR of a 1:2 mixture of [$Zn_2CuCp^*_3$] and [$Cp^*Zn_2(Et_2O)_3$][BAr_4^F] at temperatures between (-50) – 18 °C in flourobenzene/C_6D_6 (90:10 Vol%).



Scheme S2 Systematic determination of the composition and the assignment of Zn/Cu to the correct position in the molecular structure of **2**. The Cp* rings in the isomer models are omitted for clarity.

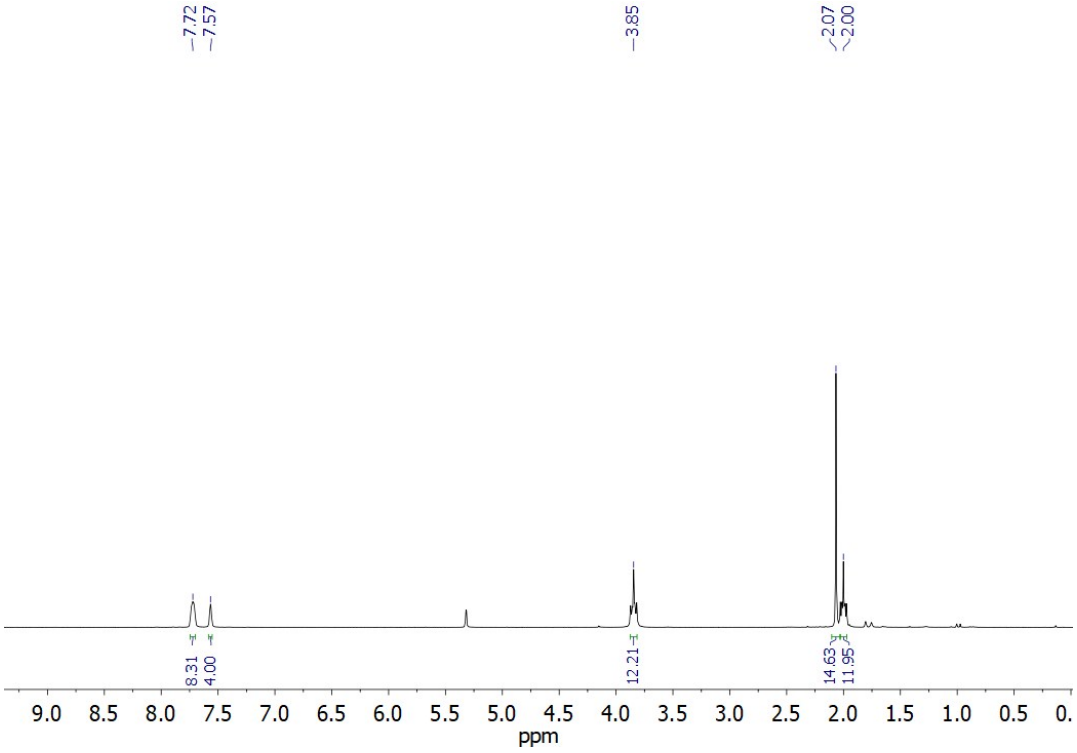


Figure S8 ^{1}H NMR spectrum of [Cp*Zn$_2$(THF)$_3$][BAr$_4^F$] recorded at room temperature in CD_2Cl_2.

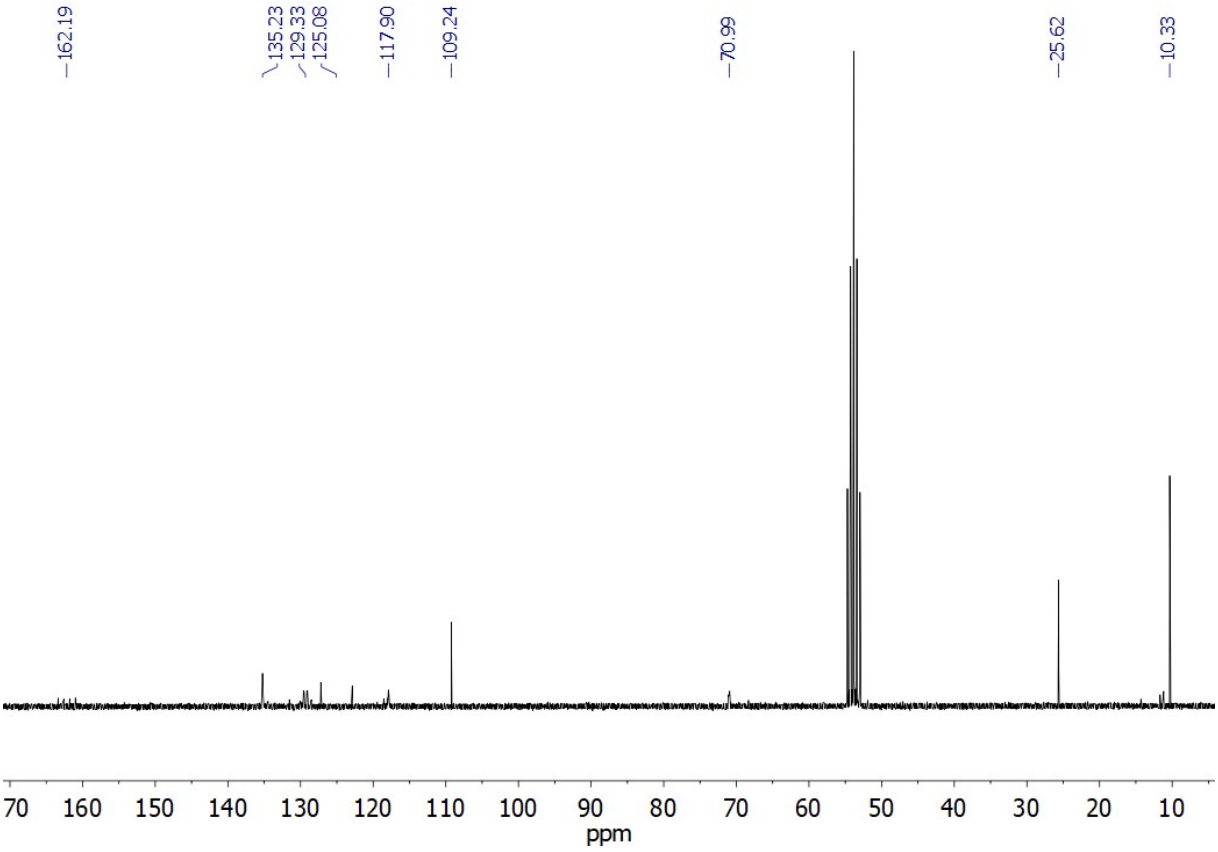


Figure S9 ^{13}C NMR spectrum of [Cp*Zn$_2$(THF)$_3$][BAr$_4^F$] recorded at room temperature in CD_2Cl_2.

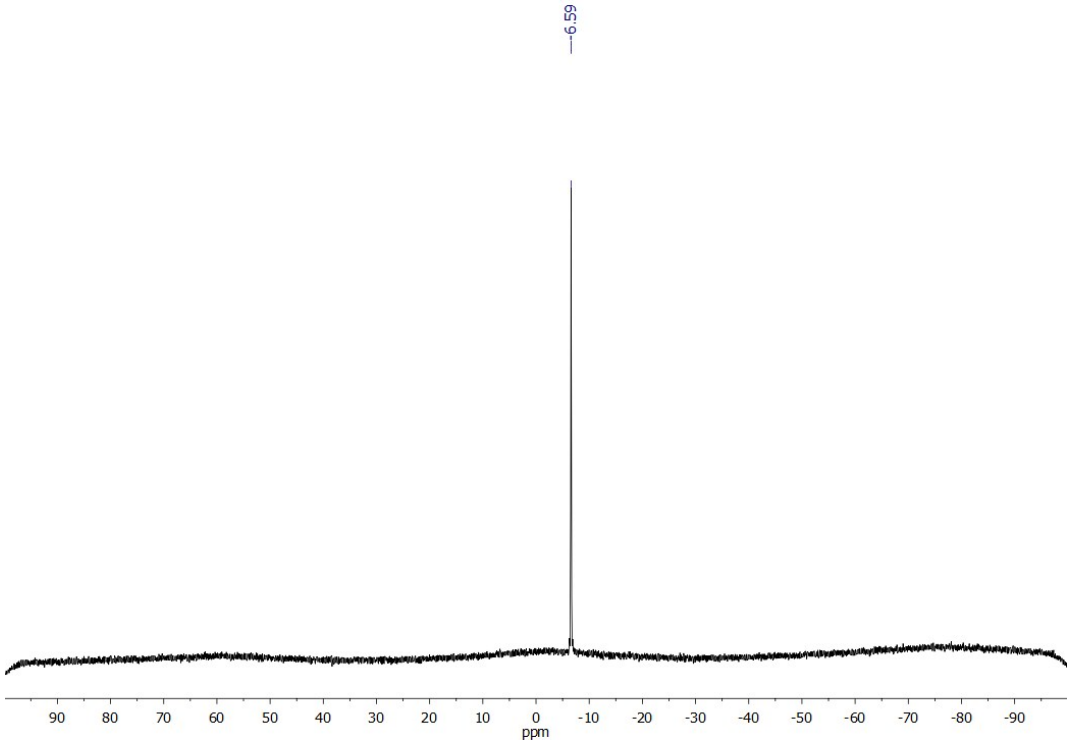


Figure S10 ^{11}B NMR spectrum of [Cp*$Zn_2(THF)_3$][BAr_4^F] recorded at room temperature in CD_2Cl_2.

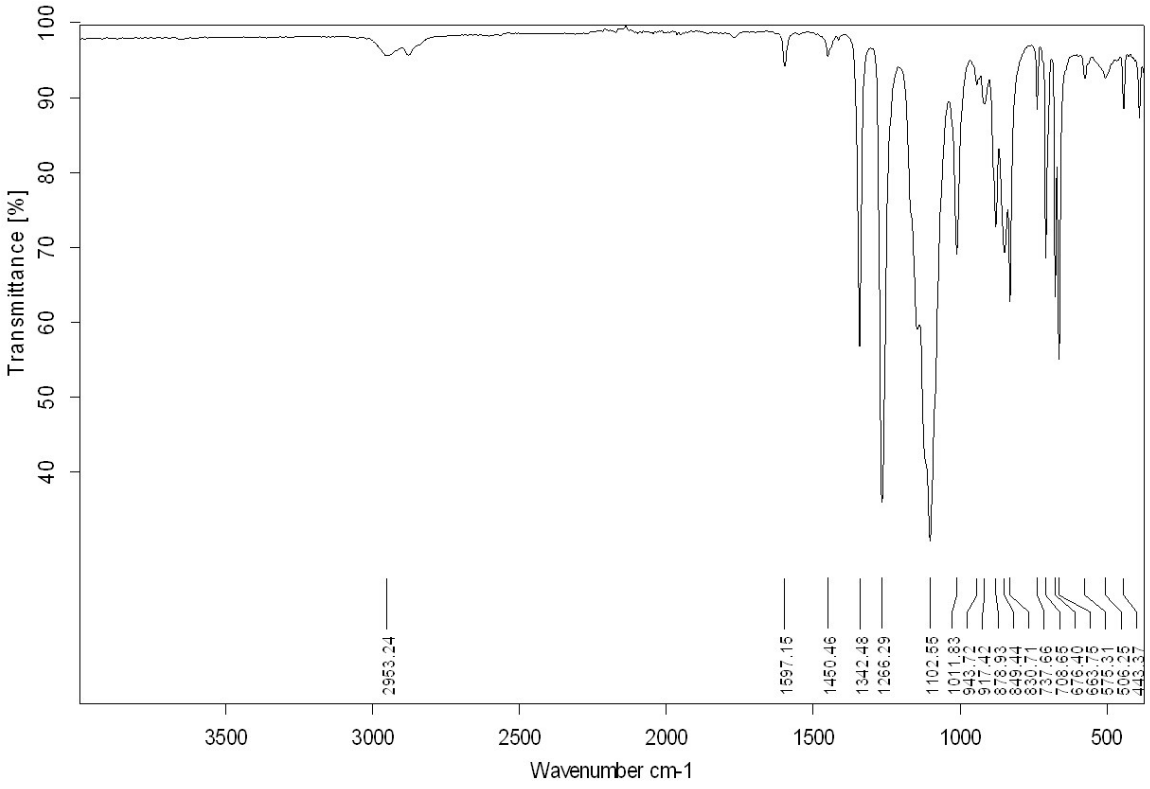
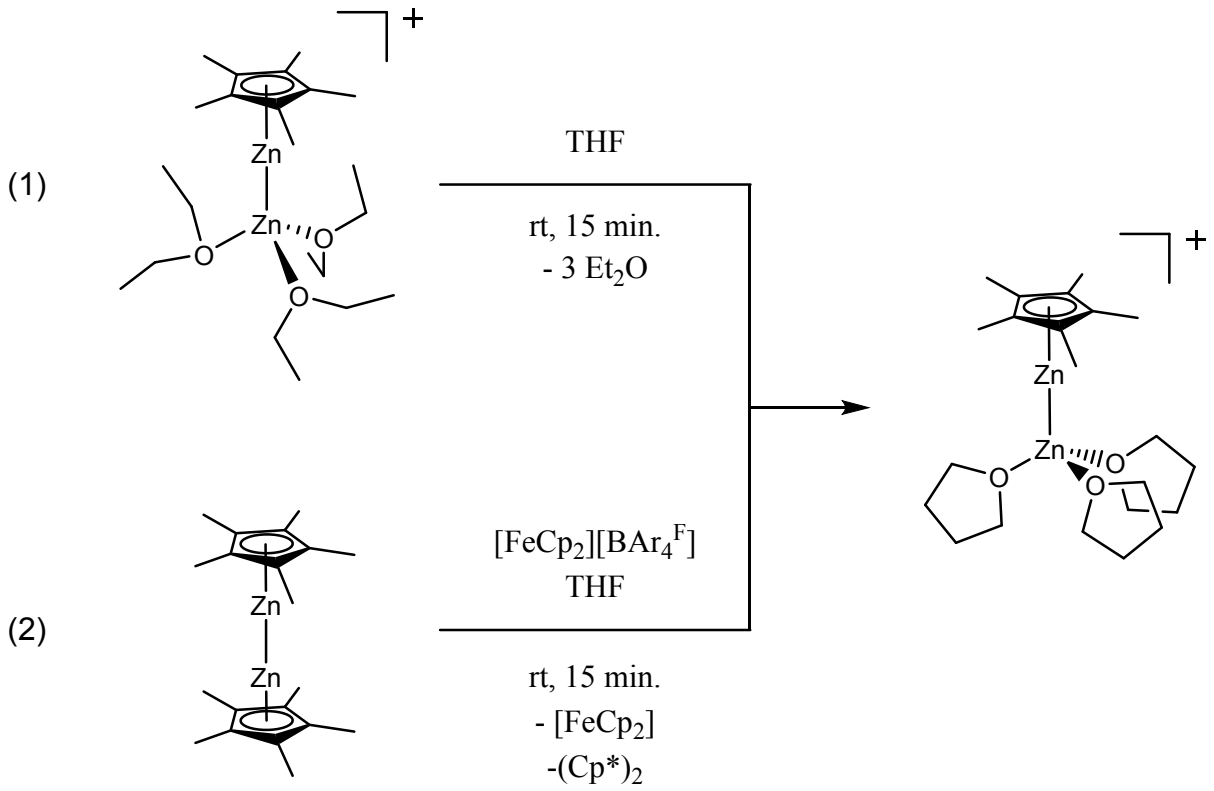
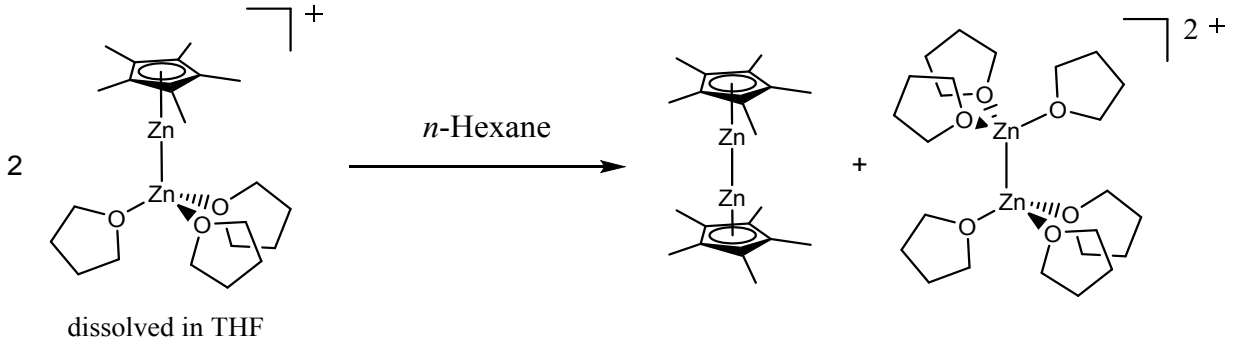


Figure S11 IR spectrum of [Cp*$Zn_2(THF)_3$][BAr_4^F].



Scheme S3 Two different pathways to synthesize $[Cp^*Zn_2(THF)_3][BAr_4^F]$.



Scheme S4 Synthesis of $[Zn_2(THF)_6][BAr_4^F]_2$ via precipitation from a THF solution of $[Cp^*Zn_2(THF)_3][BAr_4^F]$.

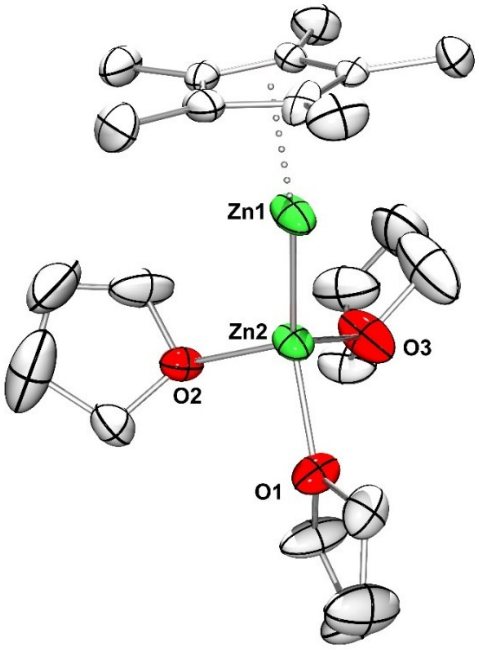


Figure S12 Priliminary molecular structure of the cation $[Cp^*Zn_2(THF)_3]^+$ in the crystal of $[Cp^*Zn_2(THF)_3][BAr_4^F]$. Displacement ellipsoids are shown at a 50 % probability level. The hydrogen atoms and the disorder of the Cp* ring are omitted for clarity. Zn1-Zn2 = 2.317(7) Å. R1 = 0.0745, wR2 (all data) = 0.2170.

Computational Details

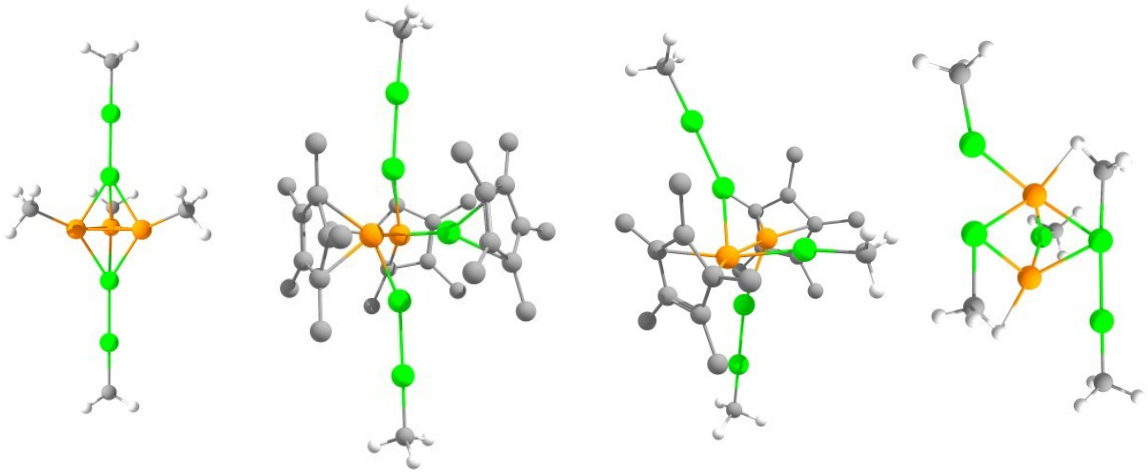
Density functional theory (DFT) calculations were carried out by using the ADF package[7-9] with the Becke-Perdew (BP86) functional[10-13] and the standard STO-TZ2P basis set. Dispersion forces were considered through the use of the empirical GDJB3 corrections of Grimme.[14] The frozen core approximation was applied to the [$1s^2$] inner electrons for C and [$1s^2$-$3p^6$] for Cu and Zn, leaving the remaining electrons to be treated variationally. Geometry optimizations were performed via the analytical energy gradient method implemented by Versluis and Ziegler.[15] The optimized geometries were characterized as true minima on the potential energy surface using vibration frequency calculations (no significant imaginary values). Wiberg indices[16] were computed with the NBO 6.0 progam.[17] Analyses of the interaction energy between fragments constituting the investigated clusters were carried out within the Morokuma-Ziegler energy decomposition analysis (EDA) formalism.[18-20] Calculations within the formalism of the quantum theory of atom in molecule (QTAIM)[21] were performed using the MULTIWFN package.[22] The calculations presented in the SI were performed using the ORCA 4.0 package[23] using the BP86-D3(BJ)/def2-TZVPP[24] level of theory, which generally shows very good agreement to the level used in the main text.

Table S2 3-fragment Morokuma-Ziegler energy decomposition analysis (EDA) of **1'** and **2'**, **1** and **2**. All values in [eV]. E_{Pauli}= Pauli repulsion; E_{elstat} = electrostatic interaction; E_{Orb} = orbital interaction. TBE = total bonding energy = $E_{\text{Pauli}} + E_{\text{elstat}} + E_{\text{orb}} + E_{\text{disp}}$.

	1'	**2'**	**1**	**2**
Fragments	$[Cu_3Cp_3]^{2-}$ + 2 $[Zn_2Cp]^+$	$[ZnCu_2Cp_3]^-$ + 2 $[Zn_2Cp]^+$	$[Cu_3Cp^*_3]^{2-}$ + 2 $[Zn_2Cp^*]^+$	$[ZnCu_2Cp^*_3]^-$ + 2 $[Zn_2Cp^*]^+$
E_{Pauli}	13.42	9.37	16.43	13.09
E_{elstat}	-21.28	-11.21	-21.41	-12.93
E_{orb}	-10.16	-7.42	-11.78	-9.18
E_{disp}	-1.30	-1.21	-2.64	-2.57
TBE	-19.32	-10.48	-19.40	-11.58

Substitution of Cp* ligands by CH_3 groups

Because the strong π-donor Cp* ligand is crucial for the stability of **1** and **2** under experimental conditions, its general influence on the core geometry of cluster **1** and **2** was evaluated. Regarding this, the synthetic boundaries and the difficult accessibility of kinetically highly labile organometallic compounds missing bulky ligands can be overcome. Thus, the Cp* ligands in **1** and **2** were systematically substituted by methyl groups without changes in the metal core geometry and geometry optimizations were performed (Figure S13). While the substitution of all Cp* groups in **1** giving $[Zn_4Cu_3Me_5]$ (**1-Me$_5$**) does not lead to major changes in the cluster geometry, the respective geometry optimization of $[Zn_5Cu_2Me_5]^+$ (**2-Me$_5$**) leads to a disintegrated metal arrangement. **1-Me$_5$** was found to be a local minimum at the BP86-D3(BJ)/TZVPP level of theory with a HOMO-LUMO gap of 1.62 eV, making it a potentially stable derivative of **1** (however most likely not under experimental conditions, due to kinetic instability). In order to specifically locate, where the presence of a Cp* group is crucial for the stability of **2**, stepwise exchange of the Cp* ligands was investigated. The replacement of the two apical ZnZnCp* groups by ZnZnMe yielding $[(\mu_3\text{-}ZnZnMe)_2(ZnCu_2Cp^*_3)]^+$ (**2-Me$_2$**) does not lead to major changes in the geometry of the metal core. This is in agreement to the discussion in the main text, where we pointed out, that only the orbitals of the terminal Zn of ZnZnR contribute to cluster bonding. Additional substitution of the basal ZnCp* group by ZnMe giving $[[(\mu_3\text{-}ZnZnMe)_2(ZnMeCu_2Cp^*_2)]^+$ (**2-Me$_3$**) leads to an elongation of the Zn3-Zn2/Zn3-Zn4 distances. This could result from a combination of the lack of dispersion forces of the Cp* groups (see main text). Moreover, the Cp*Cu-CuCp* unit is almost linear in **2-Me$_3$**. Investigating the bonding of the $(ZnR)^+$ units (R = ZnMe or Me) to the central $(Cu_2Cp^*_2)^{2-}$ unit in **2-Me$_3$** using the EDA-NOCV-method shows, that Cu-Cu π-type orbitals each interacting with the LUMO of the respective ZnR are the main orbital contributions to the Cu-ZnR bonds (Figure S 14). From this point of view, the bonding situation in **2** could also be described by three $(ZnR)^+$ units, each coordinating to occupied π/π* orbitals of the $(Cu_2Cp^*_2)^{2-}$ unit. A similar coordination mode was found recently, where a diborene unit was coordinated by three CuL^+ "ligands".[25]



1-Me_5 **2**-Me_2 **2**-Me_3 **2**-Me_5

Figure S13 Optimized structures of the Cp*/CH_3 exchanged models for **1** and **2**. Starting from the optimized structures of **1** and **2**, the ZnCp* groups were replaced by $ZnCH_3$. Subsequent geometry optimization was followed by frequency calculations to ensure the existence of a local minimum structure (not performed for **2**-Me_5). Whereas total Cp* substitution has no effect on the structural parameters of the metal core, subsequent substitution of the Cp* groups in **2** shows that the electronic effects of the Cp* moiety is crucial for the structure stability.

Table S3. Cartesian coordinates of the DFT-computed molecules.

$[Zn_4Cu_3](Cp^*_5)$ (1)

Zn	10,720529	-4,283636	-4,889554
Zn	5,368098	2,431962	-4,922321
Cu	8,621746	-0,489514	-6,086636
Zn	9,277645	-2,475984	-4,817192
Cu	8,527140	-0,498608	-3,651654
Zn	6,781621	0,601926	-4,955295
Cu	6,941515	-1,821785	-4,935382
C	12,159684	-5,452581	-6,260733
C	10,128584	-6,979770	-6,859797
C	5,969316	5,183324	-3,019510
C	4,785001	-2,073692	-5,278776
C	5,948011	-3,391546	-3,754775
C	6,221974	-3,888163	-5,081287
C	3,797041	-1,096280	-5,838317
C	4,477410	-1,463823	-2,759508
C	9,254428	1,354769	-2,687714
C	3,284006	3,322428	-4,912797
C	3,920654	3,702153	-3,682696
C	11,725732	-1,180047	-7,127045
C	5,333969	-3,381589	-7,474066
C	9,904559	-0,761451	-1,978129
C	10,316844	0,398160	-2,729729
C	11,664182	0,573605	-3,356307
C	12,847399	-5,080899	-5,056902
C	5,121658	4,646893	-5,431919
C	5,054729	4,520296	-4,003911
C	3,446023	3,357923	-2,303613
C	2,021449	2,525222	-5,041915
C	3,675916	3,826812	-7,450223
C	9,277462	-1,265842	-8,044272

C	10,380267	-0,583130	-7,404890
C	10,903434	1,902950	-6,788098
C	7,938070	2,255456	-7,867265
C	6,936661	-0,535492	-8,970296
C	9,289121	-2,701523	-8,472864
C	5,485961	-3,086140	-6,016675
C	6,441607	-4,021122	-2,490029
C	10,173106	-7,369663	-3,685612
C	12,617946	-5,670244	-2,518395
C	10,007441	0,790173	-7,228727
C	8,669514	0,955143	-7,728964
C	6,934481	1,517289	-1,491002
C	11,075142	-6,320439	-5,903671
C	11,090423	-6,488945	-4,478826
C	6,121493	5,459288	-6,197301
C	5,067930	-2,270131	-3,875212
C	6,986564	-5,133927	-5,408057
C	8,592747	-0,501233	-1,447443
C	8,181454	0,795056	-1,898269
C	10,772551	-1,938039	-1,650136
C	9,256073	2,733048	-3,273712
C	12,550681	-5,064323	-7,653952
C	12,187234	-5,721676	-3,953071
C	14,079884	-4,232113	-4,974130
C	4,027033	3,908083	-5,995420
C	7,872687	-1,352369	-0,451524
C	8,230320	-0,313745	-8,252179
H	9,157385	-7,186296	-6,391147
H	10,524904	-7,941713	-7,223759
H	9,941948	-6,352810	-7,742425
H	4,038712	-0,826917	-6,875094
H	3,776403	-0,162293	-5,258893
H	2,774960	-1,509602	-5,833062

H	4,367436	-0,407347	-3,042784
H	5,110319	-1,497661	-1,864084
H	3,479452	-1,833268	-2,472055
H	12,373422	-1,146006	-8,018705
H	11,644855	-2,232886	-6,819820
H	12,244676	-0,645242	-6,321124
H	11,659132	1,389016	-4,087676
H	11,992954	-0,336972	-3,875958
H	12,430236	0,813521	-2,600822
H	2,740714	4,112242	-1,918404
H	4,279146	3,299982	-1,590486
H	2,927521	2,389930	-2,282698
H	1,992971	1,958267	-5,982044
H	1,130717	3,174361	-5,027265
H	1,909594	1,805122	-4,220144
H	4,568440	3,890950	-8,087176
H	3,004162	4,647616	-7,750268
H	3,164489	2,885558	-7,692360
H	11,732110	1,536474	-6,171269
H	10,359960	2,661046	-6,209233
H	11,348228	2,417913	-7,656114
H	8,176710	2,750269	-8,823788
H	8,197408	2,954835	-7,061454
H	6,849200	2,113462	-7,832654
H	6,951785	-0,070979	-9,969763
H	6,085550	-0,104275	-8,424565
H	6,735162	-1,602756	-9,107965
H	9,799591	-2,833321	-9,440849
H	8,270992	-3,096101	-8,580167
H	9,808597	-3,335767	-7,739181
H	7,498850	-4,312344	-2,566469
H	5,869510	-4,931703	-2,247534
H	6,347321	-3,337673	-1,639819

H	9,184081	-7,453672	-4,155880
H	10,022435	-6,987369	-2,667065
H	10,574867	-8,391812	-3,592170
H	13,337737	-6,471583	-2,284199
H	11,767133	-5,789701	-1,834351
H	13,104687	-4,716611	-2,274015
H	6,304498	5,041546	-7,196268
H	7,088086	5,506394	-5,677664
H	5,778176	6,497306	-6,337221
H	6,333460	-6,022589	-5,389857
H	7,801989	-5,309049	-4,692633
H	7,440480	-5,079124	-6,406238
H	11,462683	-2,173693	-2,472018
H	10,177491	-2,841308	-1,461403
H	11,382045	-1,749505	-0,750670
H	9,988861	2,821792	-4,084513
H	9,505074	3,494237	-2,516438
H	8,271830	2,996507	-3,688823
H	13,057544	-4,090586	-7,678450
H	11,678938	-4,997732	-8,318804
H	13,241023	-5,799986	-8,098010
H	14,995727	-4,837357	-5,073482
H	14,144434	-3,703603	-4,013587
H	14,104878	-3,474677	-5,769175
H	6,783184	-1,254618	-0,542823
H	8,136289	-1,062865	0,579635
H	8,125429	-2,413288	-0,565986
H	4,591585	-4,180328	-7,639251
H	6,276597	-3,722236	-7,922887
H	4,994924	-2,501610	-8,032198
H	6,582350	2,191392	-2,285067
H	7,100208	2,128330	-0,588015
H	6,116087	0,819535	-1,272274

H	6,982053	5,309034	-3,425542
H	6,057678	4,603638	-2,090979
H	5,604686	6,185753	-2,741974

$[Zn_4Cu_3]Cp_5$ (1')

Cu	1,190158	0,720943	0,000000
Cu	0,021462	-1,391013	0,000000
H	0,770050	-3,242741	-2,186382
Cu	-1,222543	0,677902	0,000000
H	0,770050	-3,242741	2,186382
H	-1,802601	-3,289125	1,351231
C	-0,928181	-3,258163	-0,710876
C	0,437233	-3,220801	-1,154272
C	1,277046	-3,210502	0,000000
H	2,360789	-3,189859	0,000000
C	-2,362680	2,436090	-0,710797
H	2,417790	2,295156	-2,186333
H	1,575793	3,645546	0,000000
H	2,417790	2,295156	2,186333
H	3,746999	0,091608	1,351060
H	3,746999	0,091608	-1,351060
C	2,565979	1,996074	-1,154314
C	2,136494	2,717855	0,000000
C	2,565979	1,996074	1,154314
C	3,282337	0,833075	0,710823
C	3,282337	0,833075	-0,710823
C	-2,362680	2,436090	0,710797
C	-3,013885	1,235365	1,154272
C	-3,425551	0,503292	0,000000
C	-3,013885	1,235365	-1,154272
H	-1,951433	3,208503	-1,351007
H	-1,951433	3,208503	1,351007

H	-3,199331	0,957919	2,186283
H	-3,950357	-0,445113	0,000000
H	-3,199331	0,957919	-2,186283
H	-1,802601	-3,289125	-1,351231
C	-0,928181	-3,258163	0,710876
C	0,437233	-3,220801	1,154272
Zn	-0,003371	0,001983	-2,039313
C	0,271027	-1,193259	-6,373882
C	1,220694	-0,128823	-6,372234
C	0,502016	1,103268	-6,379038
C	-0,891999	0,800566	-6,385021
C	-1,034861	-0,618861	-6,381931
H	0,501314	-2,253252	-6,383325
H	2,299939	-0,237336	-6,379327
H	0,938897	2,095989	-6,392648
H	-1,701111	1,522748	-6,404217
H	-1,971724	-1,165303	-6,398825
Zn	0,000265	-0,003767	-4,384706
H	2,299939	-0,237336	6,379327
H	0,938897	2,095989	6,392648
C	0,502016	1,103268	6,379038
C	-0,891999	0,800566	6,385021
H	-1,701111	1,522748	6,404217
Zn	-0,003371	0,001983	2,039313
Zn	0,000265	-0,003767	4,384706
C	1,220694	-0,128823	6,372234
C	0,271027	-1,193259	6,373882
C	-1,034861	-0,618861	6,381931
H	-1,971724	-1,165303	6,398825
H	0,501314	-2,253252	6,383325

{[Zn_5Cu_2](Cp*)$_5$}$^+$ (2)

Zn	10,702580	-4,362082	-4,813096
Zn	5,247915	2,468682	-4,888170
Zn	8,534934	-0,495540	-6,057343
Zn	9,173254	-2,657644	-4,580966
Cu	8,444301	-0,524057	-3,666736
Zn	6,474849	0,525559	-4,719652
Cu	6,886476	-1,857130	-4,918502
C	12,012473	-5,510375	-6,247091
C	10,115247	-7,305947	-6,341615
C	5,659249	4,974022	-2,633457
C	4,740720	-2,155017	-5,089821
C	6,080439	-3,587252	-3,833580
C	6,254031	-3,919251	-5,231677
C	3,639225	-1,206015	-5,448674
C	4,592863	-1,899069	-2,496541
C	9,094084	1,328189	-2,730948
C	3,380884	3,603256	-5,318916
C	3,712883	3,808371	-3,933376
C	11,597820	-1,320766	-7,174833
C	5,117364	-3,188724	-7,458201
C	9,879930	-0,758751	-2,055722
C	10,202884	0,421966	-2,822030
C	11,533532	0,688778	-3,449680
C	12,837873	-4,939525	-5,215418
C	5,433121	4,699950	-5,222070
C	4,979518	4,485909	-3,875675
C	2,845743	3,465417	-2,760718
C	2,100516	3,027503	-5,842675
C	4,459006	4,258714	-7,611177
C	9,146534	-1,292827	-8,075768
C	10,284722	-0,659272	-7,455109

C	10,914414	1,807889	-6,839572
C	7,928129	2,272779	-7,817813
C	6,816457	-0,458228	-8,957098
C	9,086981	-2,733061	-8,481322
C	5,419049	-3,040649	-6,002536
C	6,686560	-4,341422	-2,691743
C	10,685447	-7,299570	-3,193900
C	13,076888	-5,252482	-2,629209
C	9,968183	0,730843	-7,262588
C	8,627718	0,951536	-7,740868
C	6,836238	1,383858	-1,410090
C	11,094685	-6,427045	-5,626071
C	11,351669	-6,423805	-4,210853
C	6,669685	5,444630	-5,622177
C	5,148158	-2,503491	-3,747193
C	7,003534	-5,101695	-5,760375
C	8,574855	-0,568269	-1,475627
C	8,083356	0,713580	-1,895534
C	10,830060	-1,871112	-1,736720
C	9,022246	2,718770	-3,281131
C	12,161839	-5,283121	-7,720111
C	12,429325	-5,503365	-3,956770
C	13,988562	-4,004022	-5,427578
C	4,446226	4,156249	-6,116578
C	7,944284	-1,465545	-0,461045
C	8,131078	-0,296620	-8,262261
H	9,256145	-7,560543	-5,707505
H	10,583179	-8,255004	-6,646963
H	9,728458	-6,829678	-7,252178
H	3,774608	-0,785357	-6,453046
H	3,575615	-0,363851	-4,746409
H	2,664752	-1,719311	-5,434095
H	4,378598	-0,829212	-2,620732

H	5,287813	-2,006992	-1,656481
H	3,649920	-2,388586	-2,207086
H	12,231357	-1,340760	-8,075287
H	11,462978	-2,360571	-6,843734
H	12,157854	-0,796551	-6,390537
H	11,485276	1,527044	-4,151148
H	11,914506	-0,186420	-3,992401
H	12,279483	0,945171	-2,681246
H	2,177835	4,302273	-2,502923
H	3,440331	3,239994	-1,865676
H	2,208239	2,595679	-2,965797
H	2,240619	2,539604	-6,815994
H	1,340790	3,812893	-5,980535
H	1,675513	2,284831	-5,155101
H	5,481279	4,300364	-8,008619
H	3,944441	5,172083	-7,948872
H	3,949858	3,408955	-8,084582
H	11,775829	1,403898	-6,297370
H	10,428847	2,559013	-6,202901
H	11,304833	2,340161	-7,721101
H	8,137719	2,777422	-8,774285
H	8,248347	2,946841	-7,013059
H	6,838914	2,160353	-7,736832
H	6,829156	0,051823	-9,932306
H	5,987781	-0,027018	-8,377915
H	6,585484	-1,511584	-9,141636
H	9,616283	-2,903803	-9,431025
H	8,052318	-3,070138	-8,615849
H	9,553204	-3,383602	-7,726891
H	7,711162	-4,671218	-2,917314
H	6,100158	-5,244912	-2,462897
H	6,722092	-3,732990	-1,781558
H	9,650891	-7,536697	-3,474647

H	10,663180	-6,829338	-2,202194
H	11,218271	-8,257306	-3,085630
H	13,901857	-5,959677	-2,449793
H	12,366437	-5,368620	-1,800456
H	13,500152	-4,241383	-2,566616
H	7,040550	5,119670	-6,602838
H	7,481595	5,309293	-4,895010
H	6,477460	6,526781	-5,692343
H	6,361493	-5,996615	-5,772169
H	7,883691	-5,337485	-5,146475
H	7,355058	-4,934376	-6,785858
H	11,521347	-2,069320	-2,566524
H	10,304821	-2,809492	-1,516789
H	11,439191	-1,620803	-0,853581
H	9,705154	2,852989	-4,128262
H	9,295657	3,460600	-2,514746
H	8,008531	2,964450	-3,629288
H	12,543821	-4,278559	-7,943755
H	11,208467	-5,404201	-8,250991
H	12,869901	-6,002253	-8,161183
H	14,925931	-4,558735	-5,590499
H	14,147996	-3,350084	-4,560227
H	13,837098	-3,363148	-6,305881
H	6,852203	-1,371138	-0,453664
H	8,295986	-1,210943	0,551513
H	8,196626	-2,518475	-0,634590
H	4,323601	-3,937776	-7,609227
H	5,992110	-3,530261	-8,024901
H	4,768487	-2,250163	-7,901884
H	6,408054	2,051688	-2,171443
H	7,045231	1,997559	-0,519757
H	6,064151	0,655124	-1,134336
H	6,751532	4,992763	-2,744120

H	5,421764	4,347193	-1,764121
H	5,343436	5,999757	-2,386263

{[Zn_5Cu_2]Cp_5}$^+$ (2')

Zn	1,367219	0,837656	0,000000
Cu	0,216820	-1,266988	0,000000
H	1,104993	-3,048767	-2,186347
Cu	-1,031190	0,765778	0,000000
H	1,104993	-3,048767	2,186347
H	-1,457946	-3,311927	1,350586
C	-0,591394	-3,183207	-0,711694
C	0,768185	-3,033968	-1,155469
C	1,604201	-2,946704	0,000000
H	2,684097	-2,857045	0,000000
C	-2,035675	2,566443	-0,711507
H	2,630156	2,455288	-2,187877
H	1,787083	3,803326	0,000000
H	2,630156	2,455288	2,187877
H	3,980918	0,266512	1,352188
H	3,980918	0,266512	-1,352188
C	2,786602	2,159394	-1,156426
C	2,346093	2,874354	0,000000
C	2,786602	2,159394	1,156426
C	3,504733	1,001655	0,713527
C	3,504733	1,001655	-0,713527
C	-2,035675	2,566443	0,711507
C	-2,772417	1,413991	1,155300
C	-3,230479	0,709164	0,000000
C	-2,772417	1,413991	-1,155300
H	-1,590295	3,319587	-1,351400
H	-1,590295	3,319587	1,351400

H	-3,003002	1,166429	2,186057
H	-3,832723	-0,191415	0,000000
H	-3,003002	1,166429	-2,186057
H	-1,457946	-3,311927	-1,350586
C	-0,591394	-3,183207	0,711694
C	0,768185	-3,033968	1,155469
Zn	-0,230399	-0,142153	-2,175655
C	-0,127147	-1,354373	-6,435122
C	0,938104	-0,401853	-6,459415
C	0,360611	0,906150	-6,456091
C	-1,061089	0,760258	-6,430257
C	-1,361661	-0,635985	-6,416771
H	-0,018148	-2,433095	-6,457858
H	1,996886	-0,630772	-6,506976
H	0,905116	1,842633	-6,500630
H	-1,784669	1,567664	-6,447135
H	-2,353520	-1,074404	-6,420181
Zn	-0,198756	-0,129213	-4,513199
H	1,996886	-0,630772	6,506976
H	0,905116	1,842633	6,500630
C	0,360611	0,906150	6,456091
C	-1,061089	0,760258	6,430257
H	-1,784669	1,567664	6,447135
Zn	-0,230399	-0,142153	2,175655
Zn	-0,198756	-0,129213	4,513199
C	0,938104	-0,401853	6,459415
C	-0,127147	-1,354373	6,435122
C	-1,361661	-0,635985	6,416771
H	-2,353520	-1,074404	6,420181
H	-0,018148	-2,433095	6,457858

$Zn_2Cu_3Cp_5$

Cu	1,093013	0,615373	0,000000
Cu	-0,099640	-1,503034	0,000000
H	0,570214	-3,389960	-2,184460
Cu	-1,331659	0,605304	0,000000
H	0,570214	-3,389960	2,184460
H	-2,004285	-3,334643	1,350069
C	-1,128588	-3,337650	-0,710584
C	0,237322	-3,355108	-1,153253
C	1,077422	-3,377742	0,000000
H	2,161132	-3,402319	0,000000
C	-2,464229	2,370353	-0,710173
H	2,316803	2,164353	-2,185389
H	1,496683	3,533131	0,000000
H	2,316803	2,164353	2,185389
H	3,623517	-0,048352	1,353250
H	3,623517	-0,048352	-1,353250
C	2,466648	1,872556	-1,152601
C	2,049285	2,600605	0,000000
C	2,466648	1,872556	1,152601
C	3,176496	0,699570	0,708303
C	3,176496	0,699570	-0,708303
C	-2,464229	2,370353	0,710173
C	-3,124307	1,173738	1,153246
C	-3,542363	0,444755	0,000000
C	-3,124307	1,173738	-1,153246
H	-2,040790	3,135940	-1,350464
H	-2,040790	3,135940	1,350464
H	-3,312909	0,896489	2,184427
H	-4,078023	-0,497616	0,000000
H	-3,312909	0,896489	-2,184427
H	-2,004285	-3,334643	-1,350069

C	-1,128588	-3,337650	0,710584
C	0,237322	-3,355108	1,153253
Zn	-0,107125	-0,098261	-2,008726
C	0,958129	-0,732876	-4,166183
C	1,658845	0,464034	-4,366720
C	0,733401	1,542294	-4,372093
C	-0,557421	1,032872	-4,174625
C	-0,449305	-0,406575	-4,027569
H	1,374971	-1,734594	-4,152707
H	2,736555	0,554411	-4,468746
H	0,985063	2,593197	-4,484273
H	-1,484213	1,596985	-4,168756
H	-1,270198	-1,111873	-4,130508
H	1,374971	-1,734594	4,152707
H	2,736555	0,554411	4,468746
H	0,985063	2,593197	4,484273
C	0,733401	1,542294	4,372093
C	-0,557421	1,032872	4,174625
H	-1,484213	1,596985	4,168756
Zn	-0,107125	-0,098261	2,008726
H	-1,270198	-1,111873	4,130508
C	1,658845	0,464034	4,366720
C	0,958129	-0,732876	4,166183
C	-0,449305	-0,406575	4,027569

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