Supporting Information

Well-defined Butadienyl Organocopper(I) Aggregates from Zirconacyclopentadienes and CuCl: Synthesis and Structural Characterization

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Contents:

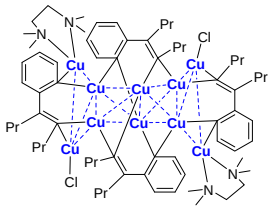
1) Experimental Details and Characterization Data

General information: Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by Mbraun SPS-800 Solvent Purification System. ^{n}BuLi was obtained from Acros. All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C), or a Bruker AVANCE III spectrometer (FT, 500 MHz for ^{1}H; 126 MHz for ^{13}C) at room temperature, unless otherwise noted. The NMR spectra of all these copper(I) aggregates contained some peaks of H grease (1.29 ppm)[1] and solvents (Hexane or Et_2O).

Procedures and Characterization Data

A typical procedure for the preparation of 2: Under an atmosphere of nitrogen, CuCl (3.0 mmol, 297.0 mg) was added to the solution of dipropyl styrenyl zirconacyclopentadiene **1** (1.0 mmol, 407.7 mg) in 6 mL THF/TMEDA (1:1) at -78 °C. After the reaction mixture was stirred for 6 h at -15 °C, solvents were removed in vacuo to give a deep red spumescence solid. The crude product was extracted with Et_2O/THF and recrystallized in Et_2O/TMEDA at -20 °C for two weeks in Glovebox to give complex **2** as air- and moisture-sensitive black crystals.

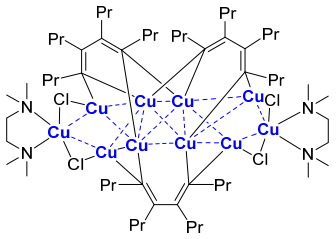


2: Black crystal, isolated yield 53% (223 mg); ^{1}H NMR (400 MHz, d^{8}-THF): δ 0.85-0.96 (m, CH_3, 24H), 1.44-1.57 (m, CH_2, 12H), 1.94-2.14 (m, CH_2, 8H), 2.31 (s, CH_3, 24H), 2.38 (s, CH_2, 8H), 2.47-2.92 (m, CH_2, 12H), 6.54-7.83 (m, CH, 16H).

A typical procedure for the preparation of 3: Compound **3** was obtained in a similar method for **2**. Under an atmosphere of nitrogen, CuCl (2.5 mmol, 247.5 mg) was added to the solution of dipropyl styrenyl zirconacyclopentadiene **1** (1.0 mmol, 407.7 mg) in 6 mL THF/TMEDA (1:1) at -78 °C. After the reaction mixture was stirred for 6 h at -15 °C, solvents were removed in vacuo to give a deep red spumescence solid. The crude product was

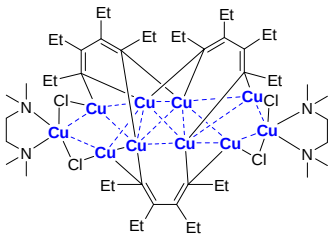
extracted with Et_2O/THF and recrystallized in Et_2O and tetrahydrothiophene at -20 °C for about two months in Glovebox to give complex **3** as air- and moisture-sensitive black crystals. The structure of **3** was elucidate by single crystal X-ray analysis.

A typical procedure for the preparation of 5: Under an atmosphere of nitrogen, CuCl (3.4 mmol, 336.6 mg) was added to the solution of tetrapropyl butadienyl zirconacyclopentadiene **4a** (1.0 mmol, 441.8 mg) in 6 mL THF at -78 °C. A yellow suspension was produced after the reaction mixture was stirred for 3 h at -20 °C. Then solvents were removed in vacuum at low temperature. The crude product was generated by adding 2.0 equiv of TMEDA after washed by hexane. Finally, complex **5**, as air- and moisture-sensitive yellow crystals, was obtained after extraction with cold THF and recrystallization in Et_2O/TMEDA at -20 °C for two weeks in Glovebox.



5: Yellow crystal, isolated yield 72%; ^{1}H NMR (500M, d^8-THF): δ 0.89-0.96 (m, CH_3, 36H), 1.10-1.70 (m, CH_2, 14H), 1.75-2.32 (m, CH_2, 19H), 2.39 (s, CH_3, 24H), 2.42 (s, CH_2, 8H), 2.44-2.74 (m, CH_2, 15H). ^{13}C NMR (126 MHz, d^8-THF) δ 15.1, 15.2, 15.4, 15.7, 15.8, 23.9, 24.1, 25.1, 26.0, 26.7, 28.3, 35.9, 36.4, 37.9, 40.6, 41.5, 41.8, 48.5, 59.0, 136.7, 137.4, 141.3, 170.4, 174.0, 179.2.

A typical procedure for the preparation of 6: Under an atmosphere of nitrogen, CuCl (3.4 mmol, 336.6 mg) was added to the solution of tetraethyl butadienyl zirconacyclopentadiene **4b** (1.0 mmol, 385.7 mg) in 5 mL THF at -78 °C. A yellow suspension was produced after the reaction mixture was stirred for 10 min at -15 °C. Then solvents were removed in vacuum at low temperature. The crude product was generated by adding 2.0 equiv of TMEDA after washed by hexane. Finally, complex **6**, as air- and moisture-sensitive yellow crystals, was obtained after extraction with cold toluene and recrystallization in THF/TMEDA at -20 °C for one month in Glovebox.



6: Yellow crystal, isolated yield 51%; ^{1}H NMR (500M, d^8-THF): δ 0.87- 0.91 (m, CH_3, 6H), 0.96-0.99 (m, CH_3, 6H), 1.04-1.10 (m, CH_3, 12H), 1.16-1.19 (m, CH_3, 12H), 1.64-1.73 (m, CH_2, 2H), 1.76-1.80 (m, CH_2, 1H), 1.87-1.96 (m, CH_2, 2H), 2.01-2.10 (m, CH_2, 5H), 2.14-2.35 (m, CH_2, 8H), 2.42 (s, CH_3, 24H), 2.44 (s, CH_2, 8H), 2.55-2.62 (m, CH_2, 3H), 2.75-2.87 (m, CH_2, 3H).

A typical procedure for the formation of 7 and 8:

Under an atmosphere of nitrogen, complex **5** (0.1 mmol, 167.1 mg), TMEDA (1.0 mmol, 116.2 mg) and THF (10 mL) were added to 25 mL Schlenk tube at -78 °C and then heated to 50 °C for 3 h. The reaction was quenched by 3 N HCl and extracted by EA. Solvents were removed under reduced pressure and the residue was purified by silica-gel to afford tricycle[4.2.0.$0^{2,5}$]octa-3,7-diene **7** as white solid. The NMR spectra of **7** are identical to the reported data.[2,3]

Under an atmosphere of nitrogen, complex **5** (0.1 mmol, 167.1 mg) was dissolved in THF (10 mL) at -78 °C, then treated with DMPU (1.0 mmol, 128.2 mg), LiCl (1.0 mmol, 42.4 mg), and 1,2-diiodobenzene (0.4 mmol, 132 mg). After stirring at 50 °C, the reaction was quenched by 3 N HCl and extracted by EA to give the crude product which was purified by silica-gel to give multisubstituted naphthalene **8**. The NMR spectra of **8** are also identical to the reported data.[4]

Reference

(1) Flulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallic* **2010**, *29*, 2176-2179.

(2) Li, G.; Fang, H.; Xi, Z. *Tetrahedron Lett*. **2003**, *44*, 8705-8708.

(3) Ubayama, H.; Sun, W.-H.; Xi, Z.; Takahashi, T. *Chem. Commun*. **1998**, 1931-1932.

(4) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc*. **1996**, *118*, 5154-5155.

2) X-ray Crystallographic Studies of 2, 3, 5, 6

The single crystals of **2** and **5** suitable for X-ray analysis were grown in Et_2O and TMEDA at -20 °C. The single crystals of **3** suitable for X-ray analysis were grown in Et_2O and tetrahydrothiophene at -20 °C. The single crystals of **6** suitable for X-ray analysis were grown in THF and TMEDA at -20 °C. Data collections for **2**, **3**, **6** were performed at 180 K on a SuperNova diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collections for **5** were performed at 173 K on a RIGAKU CCD SATURN724 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures of **2**, **3**, **5** and **6** were solved with the olex2 solve structure solution program using Charge Flipping and refined with the ShelXL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2**, **3**, **5** and **6** are summarized in Table S1–Table S4. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1410853 (**2**), CCDC 1410834 (**3**), CCDC 1410836 (**5**) and CCDC 1412019 (**6**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for 2

Identification code	**2**
Empirical formula	$C_{68}H_{104}Cl_2Cu_{10}N_4$
Formula weight	1683.85
Temperature/K	180.00(10)
Crystal system	orthorhombic

Space group	$P2_12_12$
a/Å	12.9980(4)
b/Å	15.8415(5)
c/Å	18.0179(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3710.0(2)
Z	2
ρ_{calc}g/cm^3	1.507
μ/mm^{-1}	2.915
F(000)	1728.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.618 to 52.042
Index ranges	-16 ≤ h ≤ 13, -19 ≤ k ≤ 16, -20 ≤ l ≤ 22
Reflections collected	11888
Independent reflections	6894 [R_{int} = 0.0284, R_{sigma} = 0.0509]
Data/restraints/parameters	6894/31/388
Goodness-of-fit on F^2	1.049

Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0563, wR_2 = 0.1042
Largest diff. peak/hole / e Å^{-3}	1.05/-0.40
Flack parameter	0.369(12)

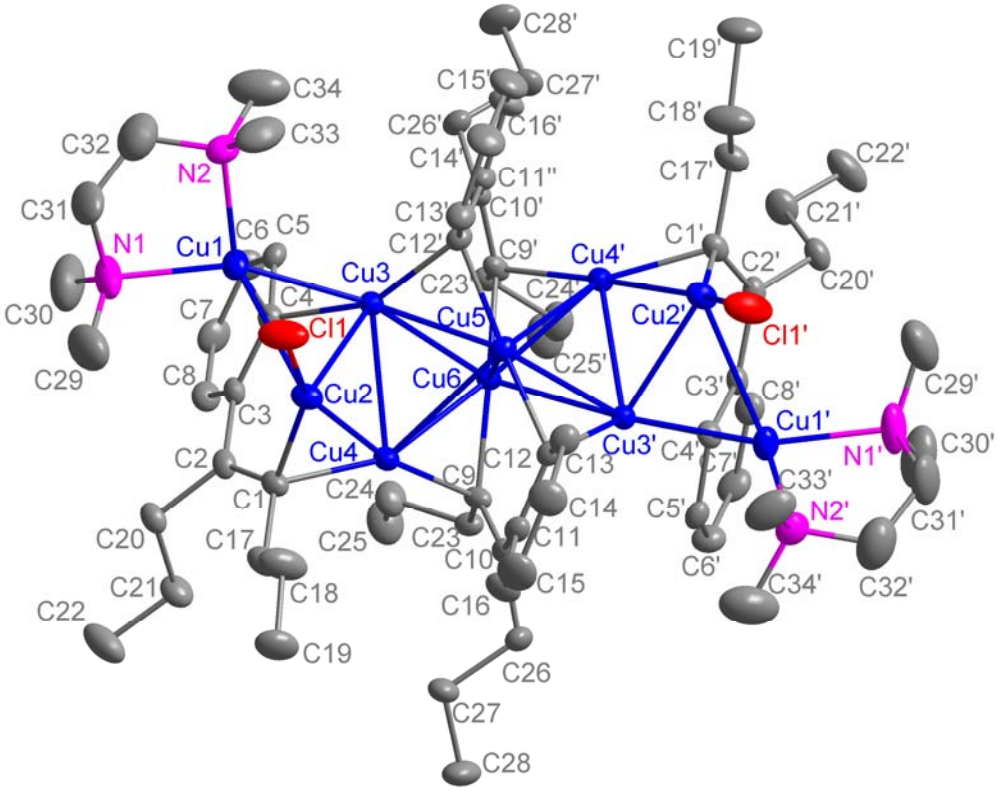


Figure S1. Diamond drawing of **2** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S2 Crystal data and structure refinement for 3

Identification code	**3**
Empirical formula	$C_{92}H_{124}Cu_{12}S_2$
Formula weight	2056.50
Temperature/K	180.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.6667(5)
b/Å	13.5072(6)
c/Å	15.0381(6)
α/°	96.035(3)
β/°	113.105(4)
γ/°	110.051(4)
Volume/Å^3	2135.82(17)
Z	1
ρ_{calc}g/cm^3	1.599
μ/mm^{-1}	3.013
F(000)	1056.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	5.922 to 52.044
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	20006
Independent reflections	8406 [R_{int} = 0.0407, R_{sigma} = 0.0606]
Data/restraints/parameters	8406/19/484
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1078
Final R indexes [all data]	R_1 = 0.0690, wR_2 = 0.1224
Largest diff. peak/hole / e $Å^{-3}$	1.47/-1.12

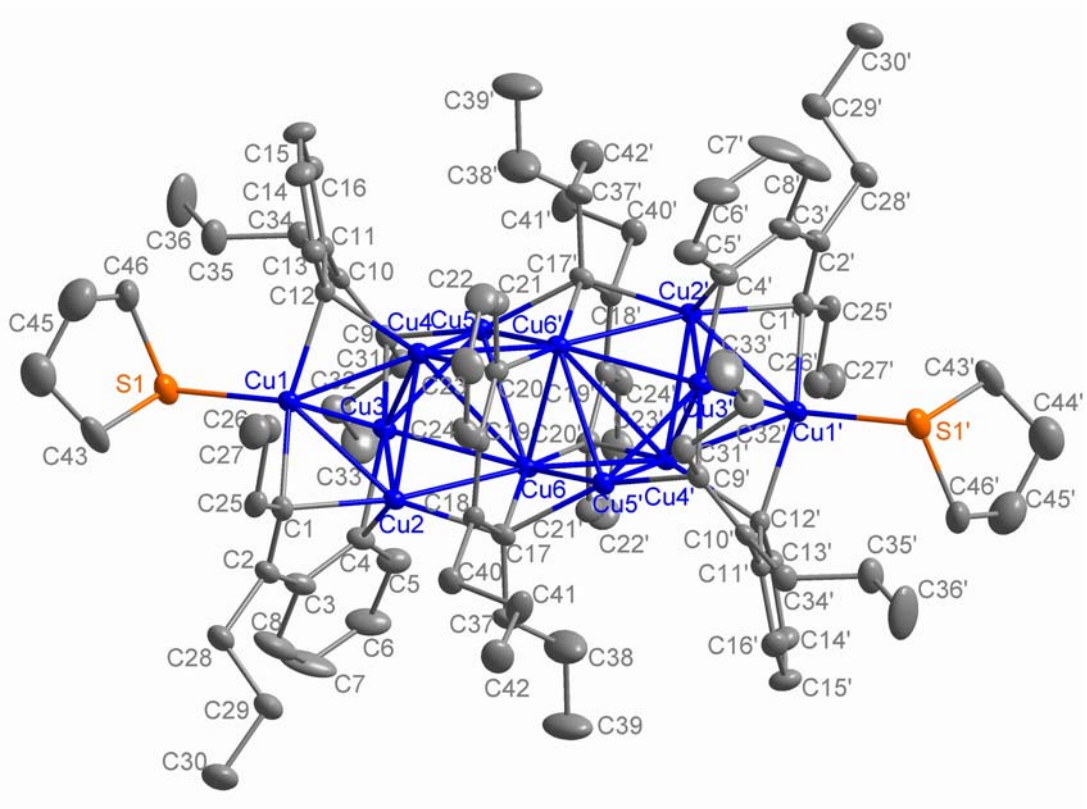


Figure S2. Diamond drawing of **3** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S3 Crystal data and structure refinement for 5.

Identification code	**5**
Empirical formula	$C_{60}H_{116}Cl_4Cu_{10}N_4$
Formula weight	1670.76
Temperature/K	173.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.307(3)
b/Å	13.054(2)
c/Å	35.207(6)
α/°	90
β/°	100.552(2)
γ/°	90
Volume/Å^3	7368(2)
Z	4
ρ_{calc}g/cm^3	1.506
μ/mm^{-1}	3.005
F(000)	3448.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	2.354 to 54.942
Index ranges	$-21 \leq h \leq 21, -16 \leq k \leq 16, -44 \leq l \leq 45$
Reflections collected	55143
Independent reflections	16813 [R_{int} = 0.0759, R_{sigma} = 0.0703]
Data/restraints/parameters	16813/69/742
Goodness-of-fit on F^2	1.178
Final R indexes [I>=2σ (I)]	R_1 = 0.0836, wR_2 = 0.2124
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.2263
Largest diff. peak/hole / e $Å^{-3}$	1.57/-0.85

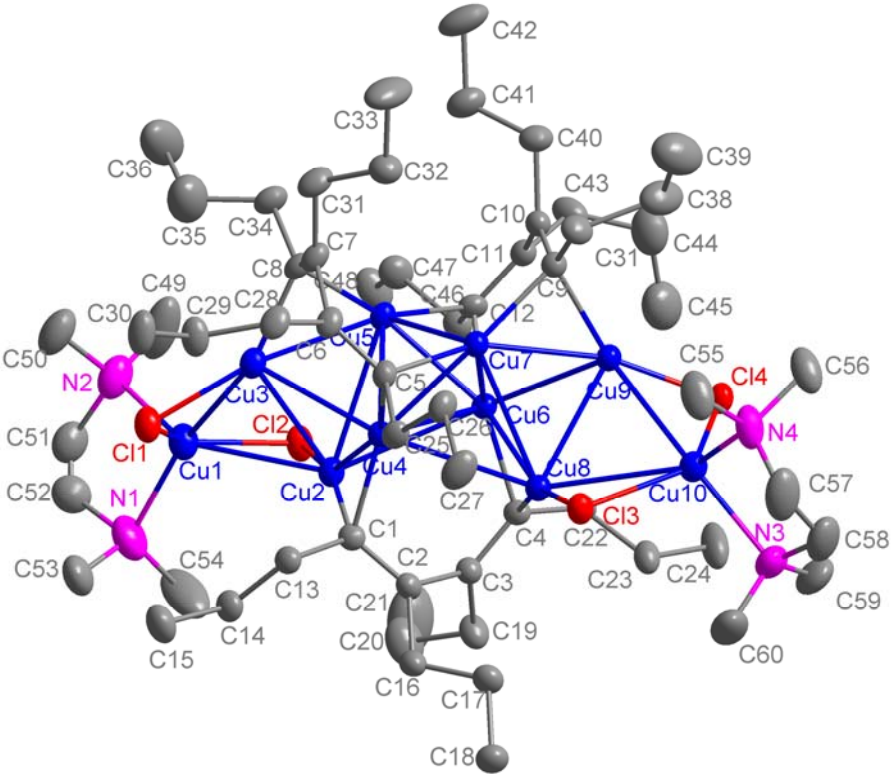


Figure S3. Diamond drawing of **5** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S4 Crystal data and structure refinement for 6

Identification code	**6**
Empirical formula	$C_{48}H_{92}Cl_4Cu_{10}N_4$
Formula weight	1502.45
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.8027(5)
b/Å	12.3566(4)
c/Å	24.9990(5)
α/°	87.633(2)
β/°	83.322(3)
γ/°	62.031(4)
Volume/Å^3	3197.8(2)
Z	2
ρ_{calc}g/cm^3	1.560
μ/mm^{-1}	3.452
F(000)	1532.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	6.018 to 52.04
Index ranges	$-13 \leq h \leq 14$, $-14 \leq k \leq 15$, $-30 \leq l \leq 30$
Reflections collected	30460
Independent reflections	12575 [R_{int} = 0.0363, R_{sigma} = 0.0601]
Data/restraints/parameters	12575/15/615
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1163
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1310
Largest diff. peak/hole / e $Å^{-3}$	1.85/-1.29

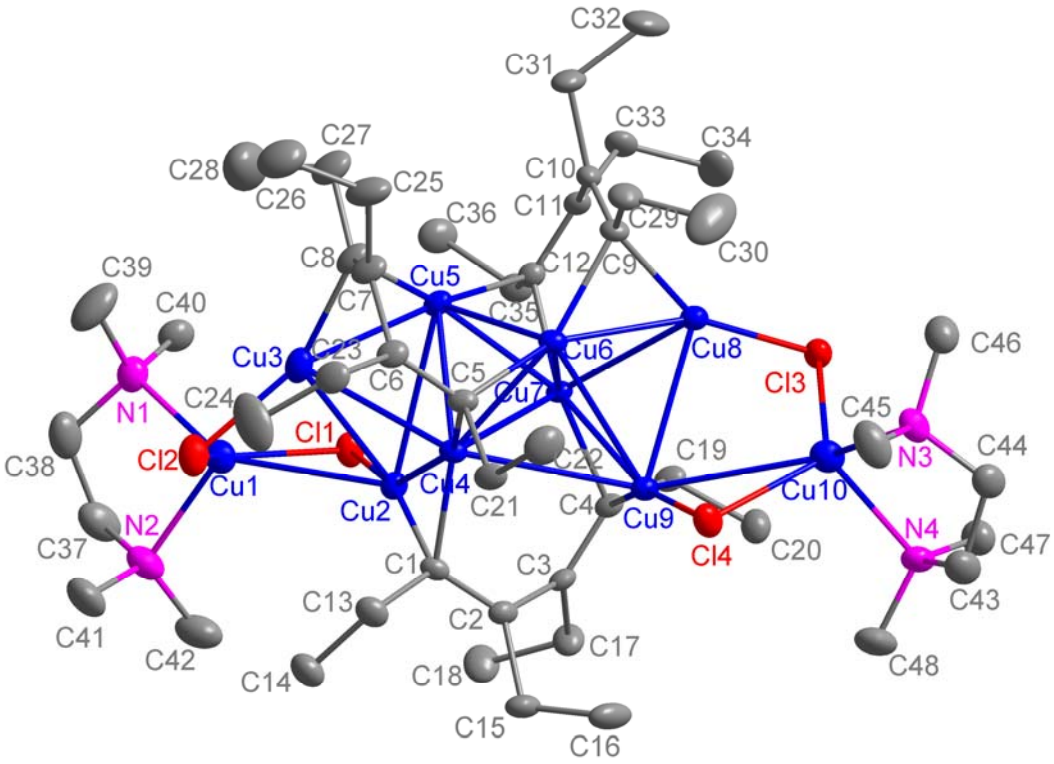
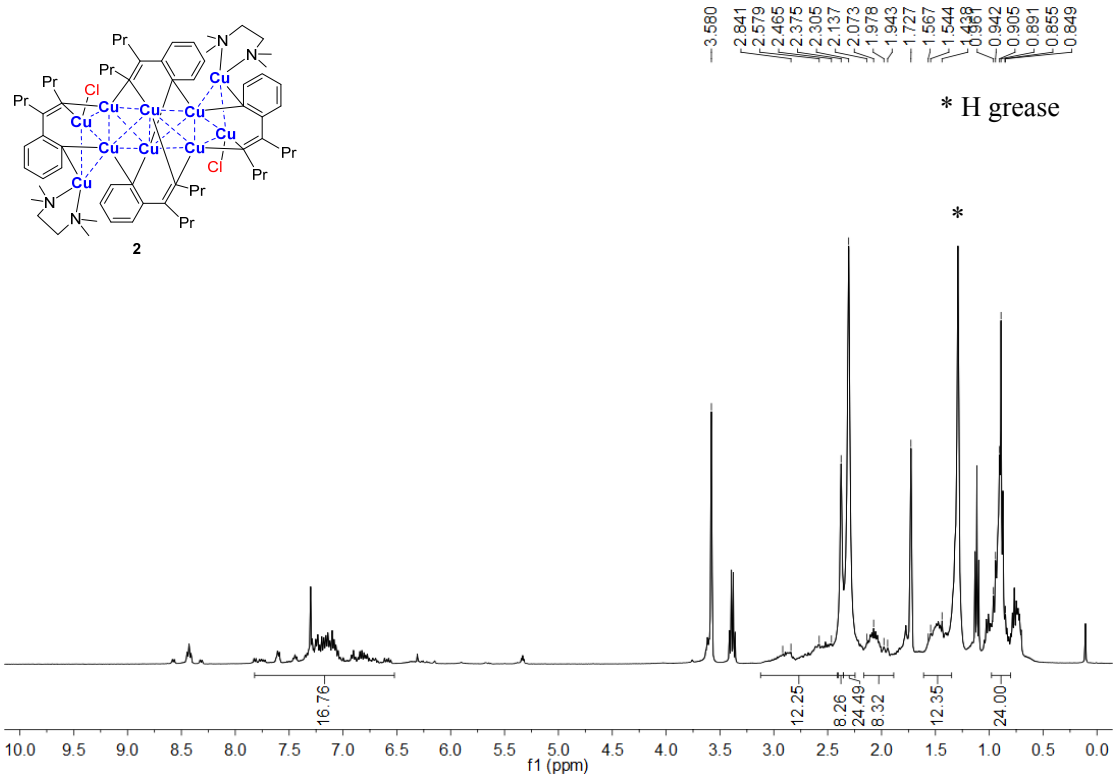


Figure S4. Diamond drawing of **6** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

3) Copies of ^{1}H NMR and ^{13}C NMR Spectra of New Compounds



2

Figure S5 ^{1}H NMR spectrum of **2**

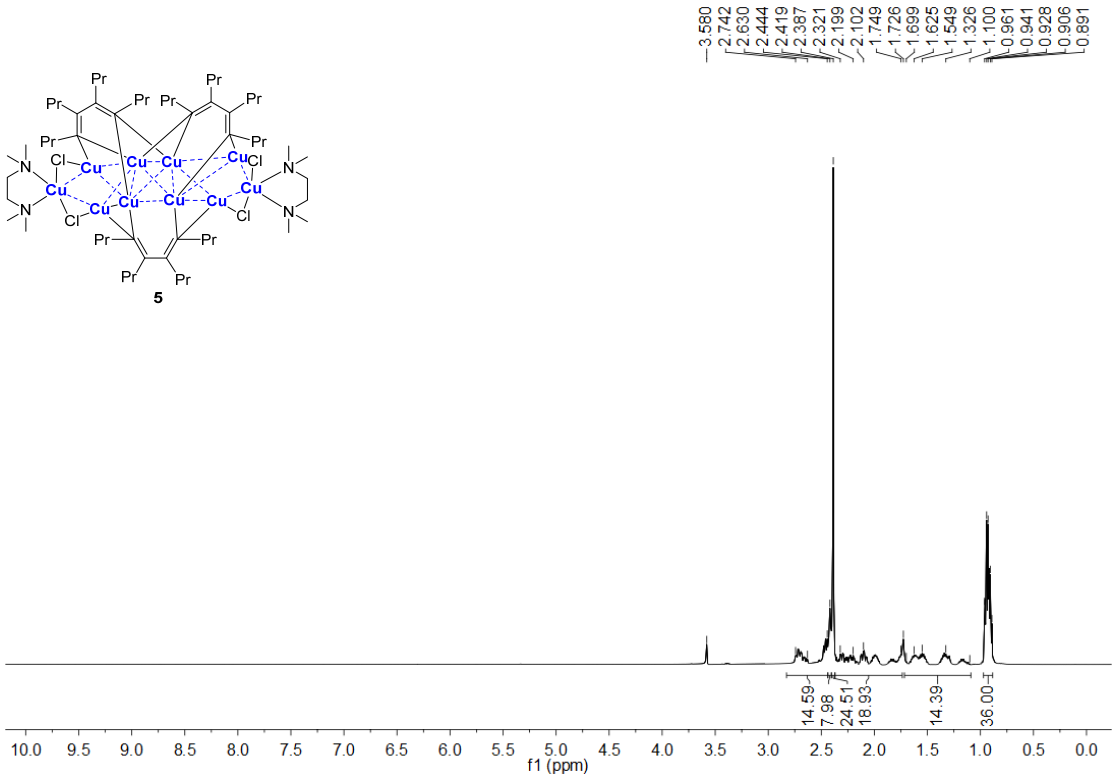


Figure S6 ^{1}H NMR spectrum of **5**

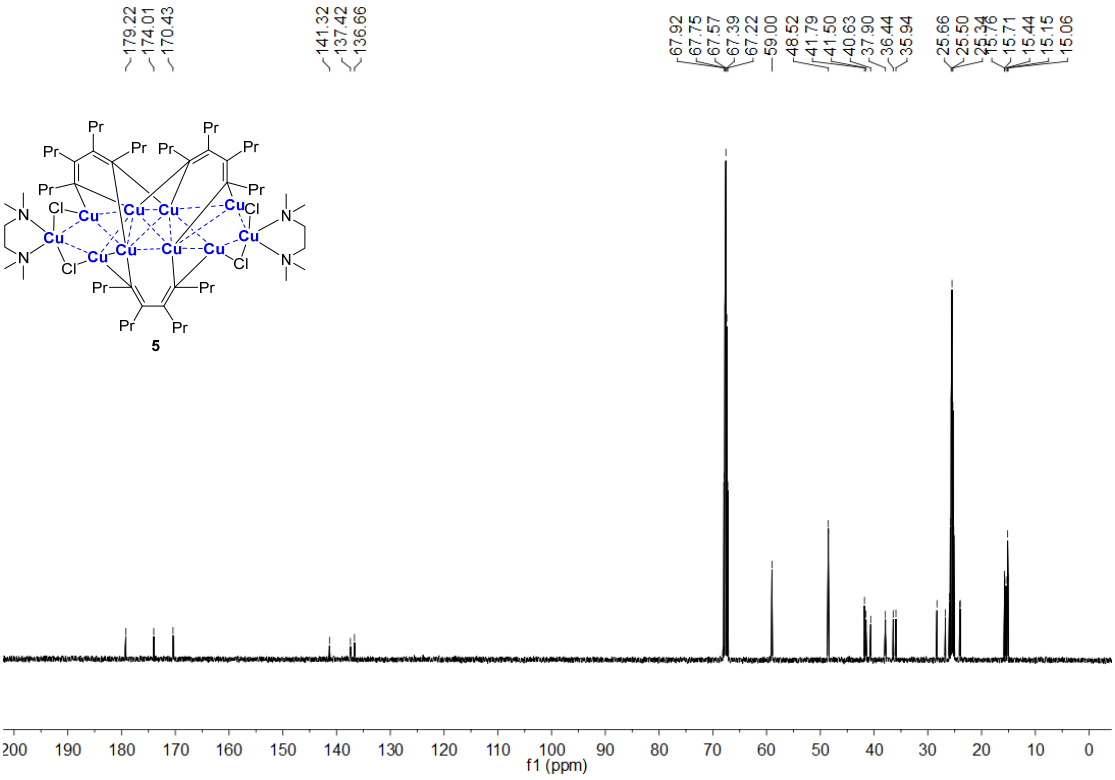


Figure S7 ^{13}C NMR spectrum of **5**

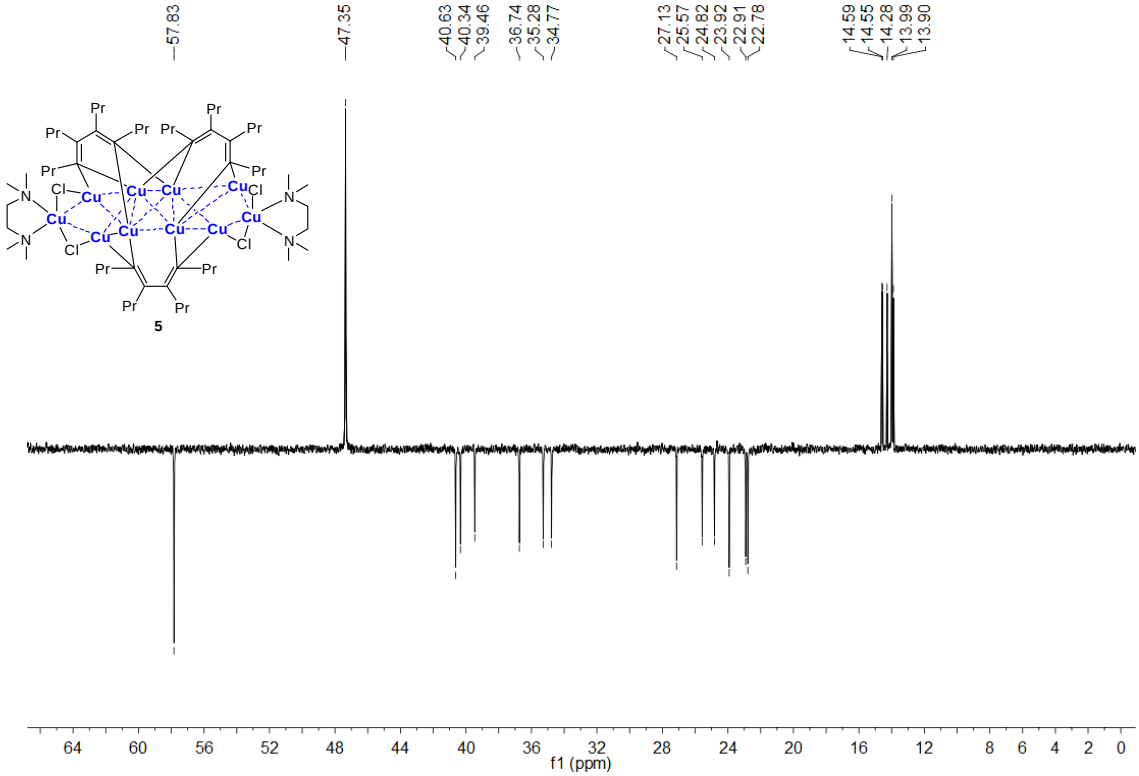


Figure S8 DEPT NMR spectrum of **5**

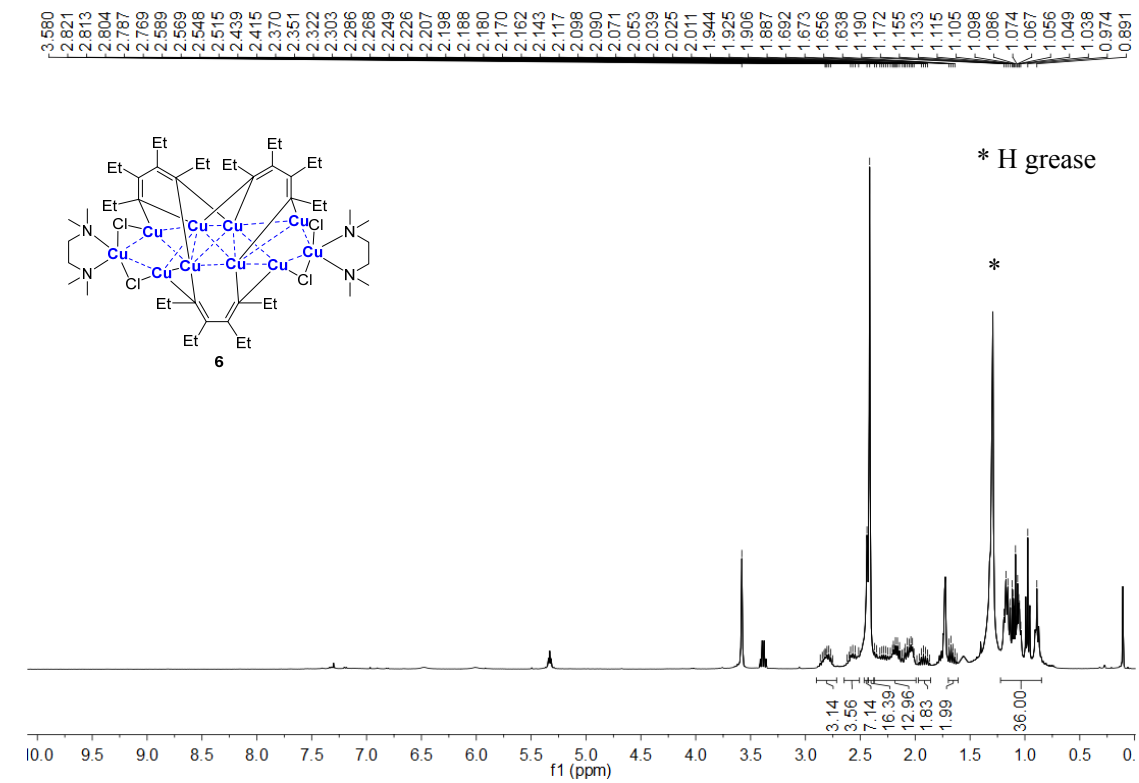


Figure S9 ^{1}H NMR spectrum of **6**