Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary material.

Halide and substituent dependent structural variation in copper(I) halide complexes of 1,5,9- triphosphacyclododecanes

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Contents

Crystallographic data.
Crystal structure determination

Single-crystal XRD data for **3** and **4** were collected on an Agilent SupaNova Dual Atlas diffractometer with a mirror monochromator using either Cu (λ = 1.5418 Å) radiation. Data for **1**, **2**, **5**, **6** and **7** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Sample temperature was maintained at 150K using an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELXS and refined using SHELXL.[i] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with Uiso set at 1.2 or 1.5 times the value of Ueq for the atom to which they are bonded. One $(CH_2)_3$ group of the ligand is disordered over two orientations in structures **1**, and **3**, with occupancies 0.72(1)/0.28(1) and 0.67(1)/ 0.33(1) respectively. All three groups are disordered in structure **7** with occupancies 0.52(2)/0.48(2), 0.566(2)/0.43(2), 0.74(1)/ 0.26(1). All disordered groups were refined with restrained geometry. The isopropyl groups in 7 display elongated displacement parameters indicative of libration. All structure figures were drawn using Ortep3v2 for Windows, ellipsoids were drawn at 35% probability for all structures.[ii] The structures deposited with the Cambridge Structural Database (CCDC deposition numbers CCDC 1558895-1558896, 1561527 and 1845379-1845382. 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 **1**, **2**, **3**, **4**, **5**, **6** and **7**

Compound (Identification code)	**1**	**2**	**3**
CCDC reference	1858170	1858168	1858173
Empirical formula	$C_{15}H_{33}Cl_2Cu_2P_3$	$C_{18}H_{39}Cl_2Cu_2P_3$	$C_{15}H_{33}Br_2Cu_2P_3$
Formula weight	504.30	546.38	593.22
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.5902(1)	7.8930(2)	8.7892(4)
b/Å	15.6586(3)	16.1790(4)	12.9061(6)
c/Å	32.0807(5)	19.5960(7)	19.9507(9)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	4315.19(12)	2502.43(13)	2263.09(18)
Z	8	4	4
Density (calculated)/ Mgm^{-3}	1.552	1.450	1.741
Absorption coefficient/ mm^{-1}	2.44	2.11	8.40
S1Crystal size/ mm^3	0.25x0.20x0.15	0.30x0.30x0.03	0.08 x 0.05 x 0.04
Reflections collected	9313	5565	5794
Independent reflections	4951	5565	3747
R(int)	0.053	0.081	0.017
Data / restraints / parameters	4951 / 110 / 231	5565 / 0 / 233	3747 / 108 / 231
Goodness-of-fit on F^2	1.02	1.04	1.05
R1, wR2 [I>2σ(I)]	0.0489, 0.0983	0.0520, 0.0919	0.0335, 0.0891
R1, wR2 (all data)	0.0727, 0.1090	0.0791, 0.1025	0.0361, 0.0921
Largest diff. peak and hole e.Å^{-3}	0.805 and -0.924	0.562 and -0.765	0.742 and -0.638

Compound (Identification code)	**4**	**5**	**6**
CCDC reference	1858169	1858172	1858171
Empirical formula	$C_{15}H_{33}BrCuP_3$	$C_{18}H_{39}BrCuP_3$	$C_{15}H_{33}ICuP_3$
Formula weight	449.77	491.85	496.76
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pna2_1$
a/Å	13.4480(3)	10.1600(2)	14.0792(6)
b/Å	10.6233(3)	15.9190(4)	10.7291(4)
c/Å	13.7607(5)	14.1560(4)	13.5869(4)
α/°	90	90	90
β/°	92.123(3)	91.038(1)	90
γ/°	90	90	90
Volume/Å^3	1964.53(10)	2289.17(10)	2052.40(13)
Z	4	4	4
Density (calculated)/ Mgm^{-3}	1.521	1.427	1.608
Absorption coefficient/ mm^{-1}	6.17	2.91	2.79
S1Crystal size/ mm^3	0.29x0.10x0.06	0.28x0.28x0.24	0.30 x 0.10 x 0.03
Reflections collected	6042	8551	4466
Independent reflections	6042	5225	4466
R(int)		0.029	0.058
Data / restraints / parameters	6042 / 0 / 184	5225 / 0 / 214	4466 / 32 / 185
Goodness-of-fit on F^2	1.15	1.03	1.111
R1, wR2 [I>2σ(I)]	0.0584, 0.1689	0.0359, 0.0668	0.0507, 0.0932
R1, wR2 (all data)	0.0622, 0.1713	0.0521, 0.0723	0.0921, 0.1106
Largest diff. peak and hole e.Å^{-3}	1.150 and -0.574	0.413 and -0.424	0.995 and -0.735

Compound (Identification code)	**7**
CCDC reference	1858174
Empirical formula	$C_{18}H_{39}CuIP_3$
Formula weight	538.84
Temperature /K	150(2)
Wavelength /Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.0360(3)
b/Å	16.1750(6)
c/Å	16.9400(6)
α/°	90
β/°	105.035(2)
γ/°	90
Volume/Å^3	2391.15(15)
Z	4
Density (calculated)/ Mgm^{-3}	1.497
Absorption coefficient/ mm^{-1}	2.40
S1Crystal size/ mm^3	0.24x0.22x0.20
Reflections collected	9491
Independent reflections	5467
R(int)	0.054
Data / restraints / parameters	5467 / 336 / 298
Goodness-of-fit on F^2	1.03
R1, wR2 [I>2σ(I)]	0.0637, 0.1203
R1, wR2 (all data)	0.1241, 0.1407
Largest diff. peak and hole e.Å^{-3}	1.400 and -0.778

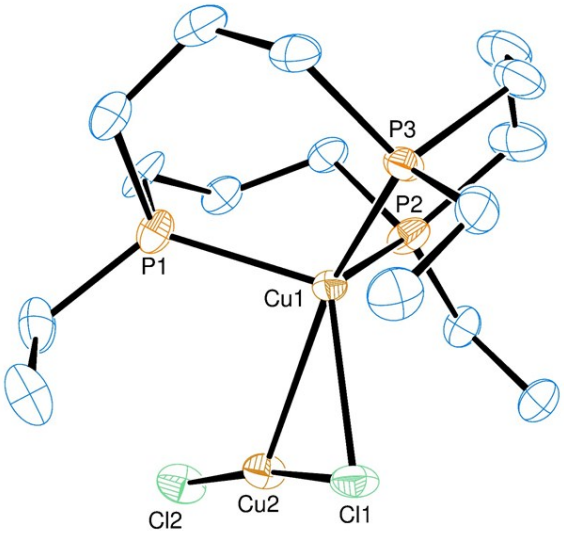

Fig 1: A 35% probability Ortep represenation of the asymmetric unit of **1** with hydrogen atoms and disordered atoms omitted.

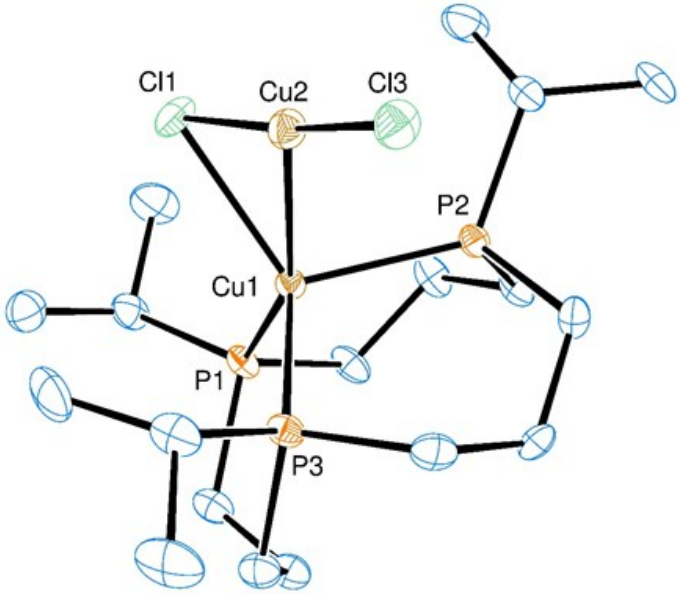

Figure 2: A 35% probability Ortep represenation of the asymmetric unit of **2** with hydrogen atoms omitted for clarity.

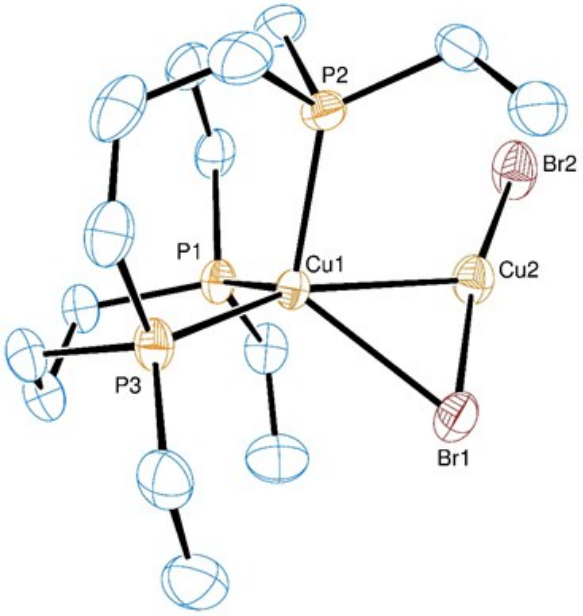

Figure 3: A 35% probability Ortep represenation of the asymmetric unit of **3** with hydrogen atoms omitted for clarity.

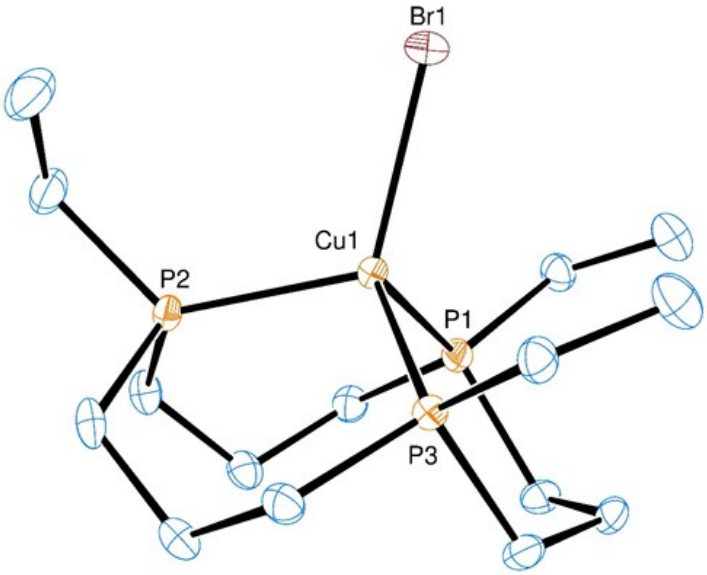

Figure 4: A 35% probability Ortep represenation of the asymmetric unit of **4** with hydrogen atoms omitted for clarity.

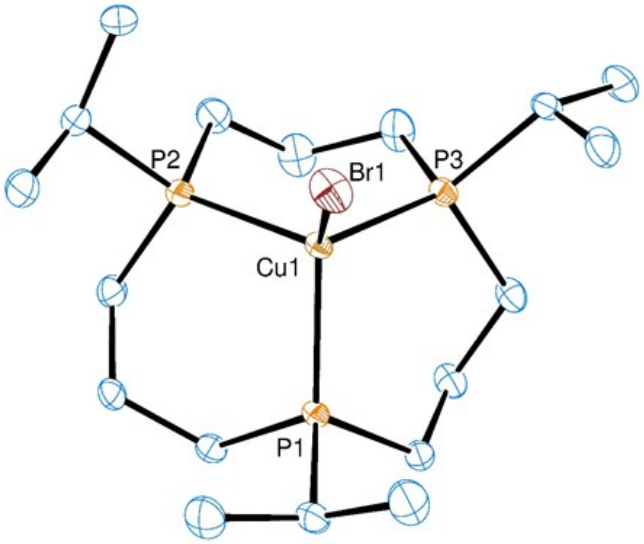

Figure 5: A 35% probability Ortep representation of the asymmetric unit of **5** with hydrogen atoms omitted for clarity.

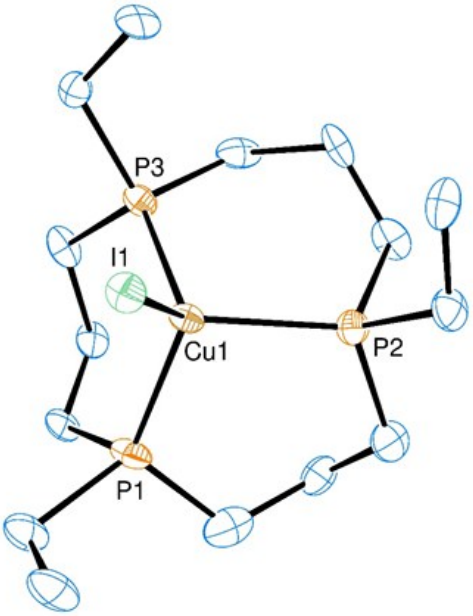

Figure 6: A 35% probability Ortep represenation of the asymmetric unit of **6** with hydrogen atoms omitted for clarity.

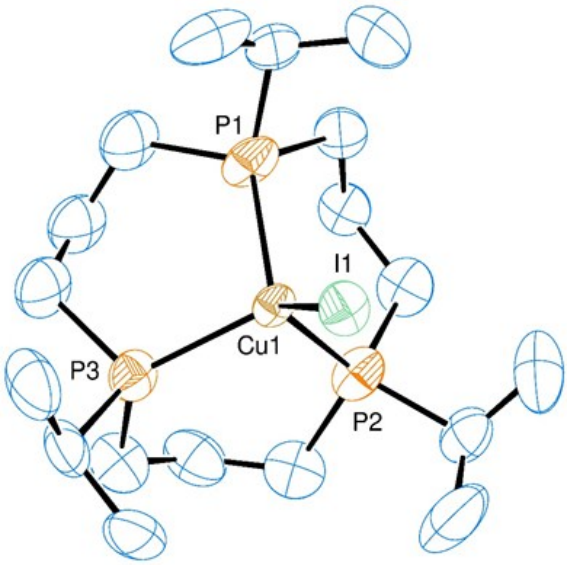

Figure 7: A 35% probability Ortep represenation of the molecular structure of **7** with hydrogen atoms and disordered atoms omitted for clarity.

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[i]) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3.

ii) L.J. Farrugia, *J. Appl. Cryst.*, 1997, **30**, 565.