Electronic Supplementary Material (ESI) for Dalton Transactions.

Copper(I) Halide Clusters Based upon Ferrocenylchalcogenoether Ligands: Donors, Halides and Semi-Rigidity Effects on the Geometry and Catalytic Activity

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Supporting Information

Table S1. Selected bond lengths (Å) and bond angles (°) for **L3** and **L4**

	Bond lengths		Bond angles	
L3	Se-C1	1.909(6)	C1-Se-C11	
	Se-C11	1.948(5)	97.87(1)	
L4	Se-C1	1.913(5)	Se-C1-Fe	122.8(3)
	Se-C11	1.982(5)	C1-Se-C11	98.9(2)
	C11-C12		Se-C1-Fe	121.6(2)
	1.492(7)		Se-C11-C12	
			113.0(3)	

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**-**6**

	Bond lengths				Bond angles			
1	Te1-Cu2	2.5985(7)	Cu1-I2	2.6894(7)	C1-Te1-Cu2	106.21(1)	$I1^{i}$-Cu1-Te2	113.56(2)
	Te1-C1	2.094(4)	$Cu1^{i}$-I1	2.5801(8)	C1-Te1-Te2	99.90(1)	$I1^{i}$-Cu1-I2	117.21(3)
	Te2-Cu1	2.5901(7)	$Cu1^{i}$-I2	2.7240(7)	Cu2-Te1-Te2	99.66(2)	Te2-Cu1-I2	101.31(2)
	Te2-C11	2.089(4)	Cu2-I2	2.7179(7)	C11-Te2-Cu1	105.14(1)	$I1^{i}$-Cu1-$I2^{i}$	112.37(2)
	Te1-Te2	2.7607(5)	Cu2-I1	2.6581(8)	C11-Te2-Te1	98.54(1)	Te2-Cu1-$I2^{i}$	108.84(2)
	$Cu1^{i}$-Cu2	2.8139(9)	Cu2-N	1.989(4)	Cu1-Te2-Te1	90.54(2)	I2-Cu1-$I2^{i}$	102.40(2)
					Cu1-I2-Cu2	93.99(2)	N-Cu2-Te2	117.35(1)
					Cu1-I2-$Cu1^{\#}$	77.60(2)	N-Cu2-I1	110.68(1)
					Cu2-I2-$Cu1^{\#}$	62.273(1)	Te1-Cu2-I1	103.43(3)
							N-Cu2-I2	106.45(1)
							Te1-Cu2-I2	108.72(2)
							I1-Cu2-I2	110.14(2)
	(i) -x, -y, -z.							
2	Te1-Cu	2.6329(1)	I-Cu	2.6192(1)	C1-Te1-C21	96.3(4)	$Te2^{iii}$-Cu-I	104.59(4)
	Te1-C1	2.095(9)	I-Cu^{i}	2.6489(13)	C1-Te1-Cu	110.4(2)	$Te2^{iii}$-Cu-Te1	102.72(4)
	Te1-C21	2.156(8)	Cu-Cu^{i}	2.805(2)	C21-Te1-Cu	103.3(3)	I-Cu-Te1	118.15(5)
	Te2-Cu^{ii}	2.6030(1)			C11-Te2-C21	94.4(4)	$Te2^{iii}$-Cu-I^{i}	119.35(5)
	Te2-C11	2.092(9)			C11-Te2-Cu^{ii}	111.3(2)	I-Cu-I^{i}	115.66(4)
	Te2-C21	2.155(9)			C21-Te2-Cu^{ii}	106.5(2)	Te1-Cu-I^{i}	96.24(4)
					Cu-I-Cu^{i}	64.34(4)	$Te2^{iii}$-Cu-Cu^{i}	134.28(7)
							I-Cu-Cu^{i}	58.34(4)
							Te1-Cu-Cu^{i}	122.90(6)

							I^{i}-Cu-Cu^{i}	57.32(4)

(i) 2-x, 2-y, 1-z
(ii) -1+x, y, z
(iii) 1+x, y, z

3	Te1-Cu	2.5736(1)	Br-Cu	2.4457(1)	C1-Te1-C21	93.98(1)	Br-Cu-Br^{ii}	109.74(3)
	Te1-C1	2.070(5)	Br-Cu^{ii}	2.5042(1)	C1-Te1-Cu	108.98(1)	Br-Cu-Te1	107.66(3)
	Te1-C21	2.154(5)	Cu-Cu^{ii}	2.8487(1)	C21-Te1-Cu	109.13(1)	Brii-Cu-Te1	120.46(3)
	Te2-Cu^{i}	2.6047(1)			C11-Te2-C21	95.67(1)	Br-Cu-$Te2^{iii}$	118.30(3)
	Te2-C11	2.091(5)			C11-Te2-Cu^{1}	109.96(1)	Br^{ii}-Cu-$Te2^{iii}$	95.98(3)
	Te2-C21	2.157(5)			C21-Te2-Cu^{i}	103.64(1)	Te1-Cu-$Te2^{iii}$	104.93(4)
					Cu-Br-Cu^{ii}	70.26(3)	Br-Cu-Cu^{ii}	55.83(4)
							Br^{ii}-Cu-Cu^{ii}	53.91(3)
							Te1-Cu-Cu^{ii}	134.92(4)
							$Te2^{iii}$-Cu-Cu^{ii}	119.91(4)

(i) -1+x, y, z
(ii) 2-x, 1-y, 1-z
(iii) 1+x, y, z

4	Se1-Cu	2.5603(1)	I-Cu	2.6046(1)	C1-Se1-C21	97.4(2)	Se2-Cu-Se1	107.61(4)
	Se1-C1	1.896(5)	I-Cu^{i}	2.6398(1)	C1-Se1-Cu	114.16(1)	Se2-Cu-I	103.74(3)
	Se1-C21	1.962(5)	Cu-Cu^{i}	2.8075(1)	C21-Se1-Cu	106.59(1)	Se1-Cu-I	115.87(3)
	Se2-Cu	2.5139(1)			C11-Se2-$C21^{ii}$	95.8(2)	Se2-Cu-I^{i}	120.20(3)
	Se2-C11	1.899(6)			C11-Se2-Cu	111.47(1)	Se1-Cu-I^{i}	94.38(3)
	Se2-$C21^{ii}$	1.969(5)			$C21^{ii}$-Se2-Cu	109.10(1)	I-Cu-I^{i}	115.27(3)
	C21-$Se2^{iii}$	1.969(5)			Cu-I-Cu^{i}	64.73(3)	Se2-Cu-Cu^{i}	133.89(5)

							Se1-Cu-Cu^{i}	118.47(4)
							I-Cu-Cu^{i}	58.24(3)
							I^{i}-Cu-Cu^{i}	57.03(3)

(i) 1-x, 1-y, -z
(ii) 1+x, y, z
(iii) -1+x, y, z

5	Se1-Cu1	2.434(2)	I1-Cu2	2.630(2)	C1-Se1-C21	101.6(5)	Se1-Cu1-I2	111.05(7)
	Se1-C1	1.921(9)	I1-Cu1^{i}	2.6642(1)	C1-Se1-Cu1	105.1(3)	Se1-Cu1-I1^{i}	104.55(6)
	Se1-C21	1.943(1)	I1-Cu1	2.6649(1)	C21-Se1-Cu1	96.1(4)	I2-Cu1-I1^{i}	111.81(5)
	Se2-Cu2^{ii}	2.401(2)	I2-Cu1	2.623(2)	C16-Se2-C21	101.7(4)	Se1-Cu1-I1	105.84(6)
	Se2-C16	1.891(9)	I2-Cu2	2.6742(1)	C16-Se2-Cu2^{ii}	107.4(3)	I2-Cu1-I1	115.24(5)
	Se2-C21	1.922(1)	I2-Cu2^{i}	2.6952(1)	C21-Se2-Cu2^{ii}	96.1(4)	I1^{i}-Cu1-I1	107.65(6)
	Cu2-Se2^{iii}	2.401 (2)	Cu1-Cu2	2.673(2)	Cu2-I1-Cu1^{i}	62.47(4)	Se1-Cu1-Cu2	146.26(7)
			Cu1-Cu2^{i}	2.745(2)	Cu2-I1-Cu1	60.64(4)	I2-Cu1-Cu2	60.65(5)
			Cu1-Cu1^{i}	2.844(3)	Cu1^{i}-I1-Cu1	64.51(6)	I1^{i}-Cu1-Cu2	108.79(7)
			Cu2-I2^{i}	2.6952(1)	Cu1-I2-Cu2	60.61(4)	I1-Cu1-Cu2	59.03(5)
			Cu2-Cu2^{i}	2.773(3)	Cu1-I2-Cu2^{i}	62.15(4)	Se1-Cu1-Cu2^{i}	146.68(7)
					Cu2-I2-Cu2^{i}	62.20(6)	I2-Cu1-Cu2^{i}	60.22(5)
							I1^{i}-Cu1-Cu2^{i}	58.15(5)
							I1-Cu1-Cu2^{i}	106.64(6)
							Cu2-Cu1-Cu2^{i}	61.56(7)
							Se1-Cu1-Cu1^{i}	141.63(5)
							I2-Cu1-Cu1^{i}	107.26(4)
							I1^{i}-Cu1-Cu1^{i}	57.75(5)
							I1-Cu1-Cu1^{i}	57.73(5)

Cu2-Cu1-Cu1^{i}	59.59(5)
Cu2^{i}-Cu1-Cu1^{i}	57.10(5)
Se2^{iii}-Cu2-I1	110.25(7)
Se2^{iii}-Cu2-Cu1	149.37(7)
I1-Cu2-Cu1	60.33(5)
Se2^{iii}-Cu2-I2	109.77(6)
I1-Cu2-I2	114.69(5)
Cu1-Cu2-I2	58.74(5)
Se2^{iii}-Cu2-I2^{i}	100.37(6)
I1-Cu2-I2^{i}	110.61(5)
Cu1-Cu2-I2^{i}	110.24(7)
I2-Cu2-I2^{i}	110.21(6)
Se2^{iii}-Cu2-Cu1^{i}	140.56(7)
I1-Cu2-Cu1^{i}	59.38(5)
Cu1-Cu2-Cu1^{i}	63.31(7)
I2-Cu2-Cu1^{i}	108.69(6)
I2^{i}-Cu2-Cu1^{i}	57.63(5)
Se2^{iii}-Cu2-Cu2^{i}	142.12(5)
I1-Cu2-Cu2^{i}	106.83(4)
Cu1-Cu2-Cu2^{i}	60.51(5)
I2-Cu2-Cu2^{i}	59.27(5)
I2^{i}-Cu2-Cu2^{i}	58.53(5)
Cu1^{i}-Cu2-Cu2^{i}	57.94(5)

(i) -1-x, -1-y, z
(ii) y, -1-x, 0.5+z
(iii) -1-y, x, -0.5+z

6	Se1-Cu1	2.446(3)	I1-Cu1^{ii}	2.586(3)	C1-Se1-C21	96.3(9)	Se1-Cu1-I1^{ii}	121.80(2)
	Se1-C1	1.920(2)	I1-Cu1	2.639(3)	C1-Se1-Cu1	111.9(7)	Se1-Cu1-I1	105.67(2)
	Se1-C21	2.00(2)	I2-Cu2	2.671(3)	C21-Se1-Cu1	103.9(6)	I1^{ii}-Cu1-I1	117.06(2)
	Se2-Cu2	2.449(3)	I2-Cu2^{i}	2.658(3)	C11-Se2-C28	96.8(7)	Se1-Cu1-Cu1^{ii}	139.5(2)
	Se2-C11	1.92(2)	I2-Cu1	2.885(4)	C11-Se2-Cu2	108.7(6)	I1^{ii}-Cu1-Cu1^{ii}	59.48(2)
	Se2-C28	2.012(2)	Cu2-N1	2.045(2)	C28-Se2-Cu2	100.6(6)	I1-Cu1-Cu1^{ii}	57.59(2)
			Cu1-Cu1^{ii}	2.728(6)	Cu1^{ii}-I1-Cu1	62.94(2)	Se1-Cu1-I2	105.82(2)
			Cu2-Cu2^{i}	2.803(6)	Cu2^{i}-I2-Cu2	63.48(2)	I1^{ii}-Cu1-I2	94.11(2)
					Cu2^{i}-I2-Cu1		I1-Cu1-I2	111.05(2)
					117.34(2)		Cu1^{ii}-Cu1-I2	114.54(2)
					Cu2-I2-Cu1	142.03(2)	N1-Cu2-Se2	106.5(6)
							N1-Cu2-I2^{i}	109.6(5)
							Se2-Cu2-I2^{i}	109.43(2)
							N1-Cu2-I2	104.3(5)
							Se2-Cu2-I2	110.0(2)
							I2^{i}-Cu2-I2	116.52(2)
							N1-Cu2-Cu2^{i}	123.5(6)
							Se2-Cu2-Cu2^{i}	129.88(2)
							I2^{i}-Cu2-Cu2^{i}	58.49(9)
							I2-Cu2-Cu2^{i}	58.04(2)

(i) 1-x, 2-y, 1-z
(ii) 1-x, 1-y, 1-z

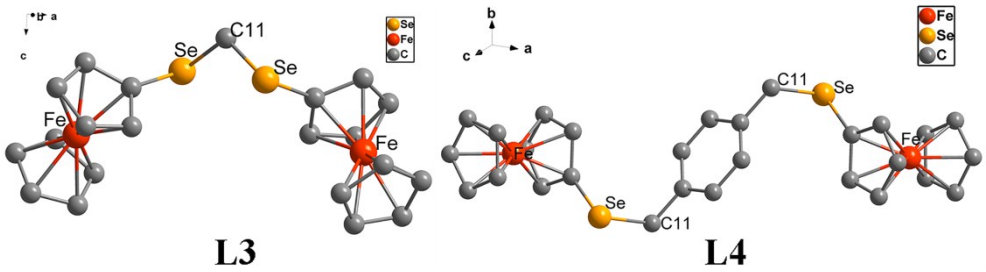

Figure S1. The molecular structures of **L3** and **L4**

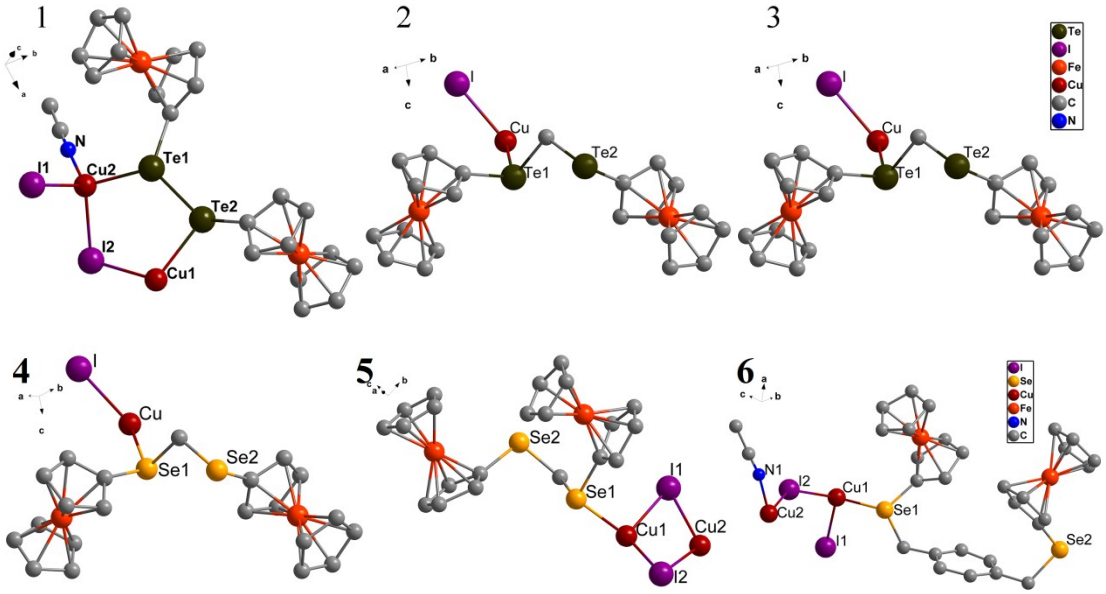

Figure S2. The asymmetric units of **1**-**6**

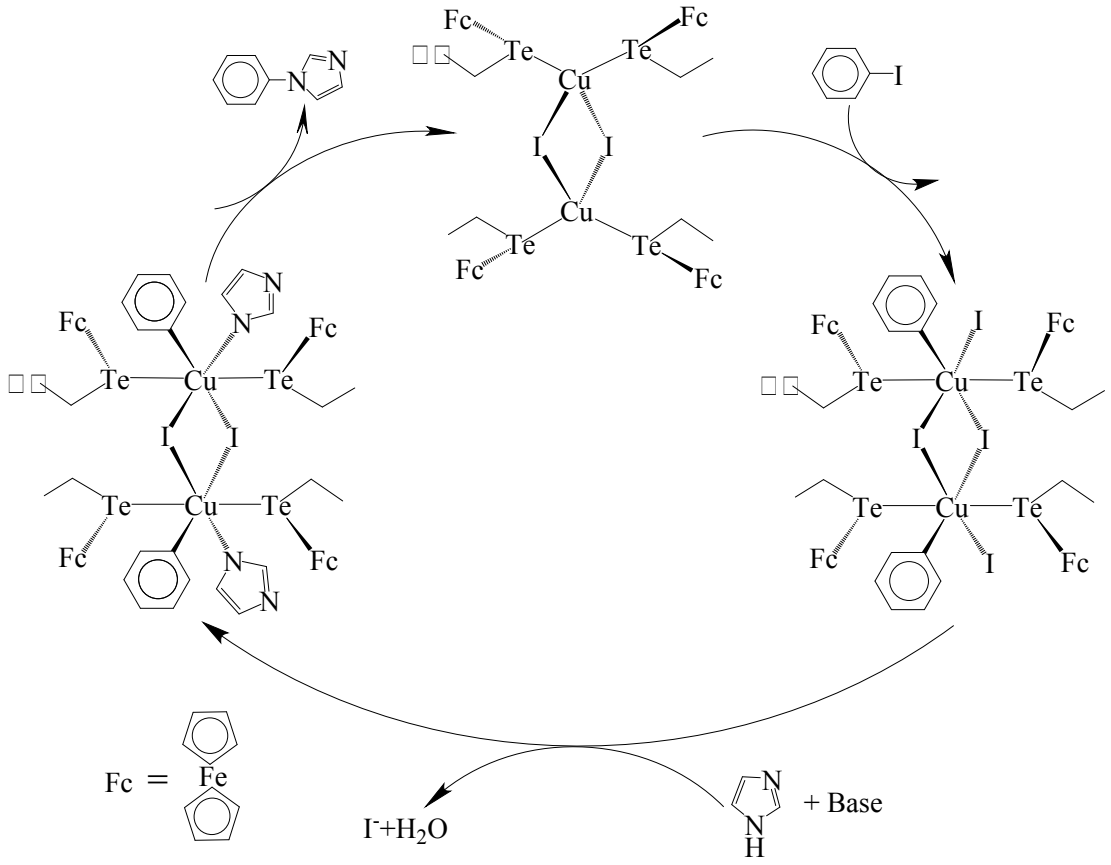

Figure S3. Outline of a possible pathway for copper(I) cluster **2** catalyzed C-N coupling reaction