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Supporting Information

Coinage Metal Coordination Chemistry of Stable Primary, Secondary and Tertiary Ferrocenylethyl-Based Phosphines

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Table S1. Crystallographic data and parameters for compounds **1-CuCl**, **3-CuCl**, **1-AgCl**, **3-AgCl**, **3-CuOAc**, **3-AgOAc**, **2-AuCl** and **3-AuCl**.[a]

	1-CuCl	**3-CuCl**	**1-AgCl**	**3-AgCl**	**3-CuOAc**	**3-AgOAc**	**2-AuCl**	**3-AuCl**
formula	$C_{48}H_{60}Cl_4Cu_4Fe_4P_4$	$C_{144}H_{156}Cl_4Cu_4Fe_{12}P_4$	$C_{48}H_{60}Ag_2Cl_2Fe_2P_2$	$C_{144}H_{156}Ag_4Cl_4Fe_{12}P_4$ ·3CH_2Cl_2	$C_{152}H_{168}Cu_4Fe_{12}O_8P_4$ ·2THF	$C_{152}H_{168}Ag_4Fe_{12}O_8P_4$ ·2THF	$C_{24}H_{27}AuClFe_2P$	$C_{36}H_{39}AuClFe_3P$ ·½THF
formul	1380.20	3076.72	1270.88	3508.82	3315.30	3492.62	690.54	938.66
crystal	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space	*C2/c*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	55.660(19)	19.202(9)	21.644(15)	16.755(3)	13.340(9)	13.356(16)	11.016(2)	15.675(4)
b [Å]	7.717(3)	25.786(10)	7.795(5)	16.972(3)	16.897(8)	16.784(18)	12.823(2)	16.981(3)
c [Å]	36.097(13)	29.561(16)	14.445(10)	26.793(6)	17.289(10)	17.332(11)	15.892(3)	17.021(3)
α [°]	90	68.256(9)	90	88.850(10)	66.770(14)	69.038(9)	85.180(10)	118.147(9)
β [°]	90.196(18)	72.394(13)	96.234(11)	83.595(6)	80.739(19)	83.27(3)	81.788(16)	91.603(7)
γ [°]	90	89.502(8)	90	65.477(7)	82.12(2)	78.13(4)	89.914(10)	115.305(8)
V [Å^3]	15504(10)	12870(11)	2423(3)	6885(2)	3523(3)	3546(6)	2213.8(8)	3458.4(13)
Z	12	4	2	2	1	1	4	4
ρ_{cal} [g	1.774	1.588	1.742	1.692	1.563	1.635	2.072	1.803
M	3.067	2.135	2.234	2.066	1.888	1.828	8.106	5.614
F(000)	8352	6304	1280	3548	1712	1784	1336	1856
tempe	110	110	110	110	110	110	110	110
ϑ_{min},	2.69, 26.31	2.60, 31.68	2.84, 28.70	2.53, 40.39	2.69, 32.40	2.73, 40.42	2.97, 29.59	2.98, 30.53
total	49572	220430	31193	268846	60131	86384	12250	32436
unique	12732	61418	6180	57583	16123	16968	12250	10825
R(int)	0.0683	0.0306	0.0641	0.0240	0.0498	0.0204	0.0434	0.0253
R_1	0.0424	0.0355	0.0438	0.0296	0.0386	0.0292	0.0542	0.0454
wR_2 [*I*	0.1120	0.1028	0.0713	0.0848	0.0991	0.0979	0.1323	0.1170
R_1 (all	0.0705	0.0534	0.0931	0.0394	0.0646	0.0361	0.0996	0.0503
wR_2	0.1496	0.1285	0.0912	0.0988	0.1377	0.1185	0.1685	0.1244
GOF	1.129	1.088	1.029	1.145	1.047	1.009	1.041	1.157

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum F_o$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^2)]^{1/2}$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{observns} - N_{params})]^{1/2}$

Table S2. Selected bond lengths [Å] with e.s.d.'s in parentheses.

1-CuCl							
Cu1-P1	2.160(2)	Cu1-Cl3	2.583(1)	Cu8-Cl7	2.637(1)	Cu1- P1	2.151(2)
Cu1-Cl1	2.356(2)	Cu2-P2	2.181(2)	Cu8-Cl8	2.321(1)	Cu1-O1	1.991(3)
Cu1-Cl2	2.371(2)	Cu2-Cl1	2.488(1)			Cu1-O2	2.148(3)
Cu1-Cl3	2.490(2)	Cu2-Cl2	2.407(1)	**1-AgCl**		Cu2-P2	2.165(1)
Cu2-P2	2.169(2)	Cu2-Cl4	2.391(1)	Ag1-Cl1	2.591(2)	Cu2-O3	2.052(3)
Cu2-Cl1	2.442(2)	Cu3-P3	2.174(1)	Ag1-P1	2.456(2)	Cu2-O4	1.982(3)
Cu2-Cl2	2.376(2)	Cu3-Cl1	2.400(1)	Ag1-P2	2.444(2)		
Cu2-Cl4	2.449(2)	Cu3-Cl3	2.400(1)			**3-AgOAc**	
Cu3-P3	2.172(2)	Cu3-Cl4	2.511(1)	**3-AgCl**		Ag1-Ag2	2.959(2)
Cu3-Cl1	2.392(2)	Cu4-P4	2.188(1)	Ag1-P1	2.3754(9)	Ag1-P1	2.369(1)
Cu3-Cl3	2.552(2)	Cu4-Cl2	2.488(1)	Ag1-Cl1	2.7063(8)	Ag1-O1	2.217(3)
Cu3-Cl4	2.349(2)	Cu4-Cl3	2.402(1)	Ag1-Cl2	2.4737(8)	Ag1-O3	2.385(4)
Cu4-P4	2.173(2)	Cu4-Cl4	2.422(1)	Ag2-P2	2.3711(8)	Ag2-P2	2.348(3)
Cu4-Cl2	2.559(2)	Cu5-P5	2.184(1)	Ag2-Cl1	2.7377(8)	Ag2-O2	2.478(4)
Cu4-Cl3	2.348(2)	Cu5-Cl7	2.371(1)	Ag2-Cl2	2.7630(8)	Ag2-O4	2.197(3)
Cu4-Cl4	2.382(2)	Cu5-Cl5	2.479(1)	Ag2-Cl4	2.5258(6)		
Cu6-P6	2.164(2)	Cu5-Cl6	2.480(1)	Ag3- P3	2.3735(7)	**2-AuCl**	
Cu6-Cl5	2.249(2)	Cu6-P6	2.178(1)	Ag3-Cl1	2.6769(6)	Au1-P1	2.236(4)
Cu6-Cl6	2.375(2)	Cu6-Cl5	2.363(1)	Ag3-Cl3	2.5148(8)	Au1-Cl1	2.309(4)
Cu5-P5	2.176(2)	Cu6-Cl6	2.398(1)	Ag3-Cl4	2.8234(8)	Au2-P2	2.235(4)
Cu5-Cl5	2.360(2)	Cu6-Cl8	2.542(1)	Ag4-P4	2.3839(8)	Au2-Cl2	2.295(4)
Cu5-Cl6	2.589(2)	Cu7-P7	2.182(1)	Ag4-Cl2	2.8308(6)		
		Cu7-Cl5	2.489(1)	Ag4-Cl3	2.5689(8)	**3-AuCl**	
3-CuCl		Cu7-Cl7	2.382(1)	Ag4-Cl4	2.6374(8)	Au2-Cl2	2.294(3)
Cu1-P1	2.168(1)	Cu7-Cl8	2.428(1)			Au2-P2	2.227(3)
Cu1-Cl1	2.417(1)	Cu8-P8	2.174(1)	**3-CuOAc**		Au1-Cl1	2.300(3)
Cu1-Cl2	2.318(1)	Cu8-Cl6	2.404(1)	Cu1-Cu2	2.799(2)	Au1-P1	2.224(2)

Table S3. Selected bond angles [°] with e.s.d.'s in parentheses.

1-CuCl		Cu3-Cl3-Cu4	82.15(5)	Cl5-Cu5-Cl6	91.16(3)	Cu5-Cl7-Cu8	80.90(2)	Ag3-Cl3-Ag4	92.88(2)
P1-Cu1-Cl3	106.85(6)	Cu4-Cl3-Cu1	85.18(6)	Cl5-Cu5-Cl7	93.87(3)	Cu7-Cl7-Cu8	81.39(2)	Ag3-Cl4-Ag4	84.78(2)
P1-Cu1-Cl1	124.84(7)	Cu2-Cl4-Cu3	85.92(6)	Cl6-Cu5-Cl7	100.31(3)	Cu6-Cl8-Cu7	80.49(2)	Ag4-Cl2-Ag1	81.44(2)
P1-Cu1-Cl2	120.35(7)	Cu3-Cl4-Cu4	85.89(6)	P6-Cu6-Cl5	123.53(4)	Cu7-Cl8-Cu8	87.28(3)	Ag4-Cl4-Ag2	93.51(2)
Cl1-Cu1-Cl2	99.70(6)	Cu4-Cl4-Cu2	81.07(6)	P6-Cu6-Cl6	126.84(4)	Cu8-Cl8-Cu6	84.57(3)		
Cl1-Cu1-Cl3	106.64(6)	Cu5-Cl5-Cu6	85.49(6)	P6-Cu6-Cl8	113.08(3)			**3-CuOAc**	
Cl2-Cu1-Cl3	93.61(6)	Cu6-Cl5-Cu6	73.78(5)	Cl8-Cu6-Cl5	98.44(3)	**1-AgCl**		Cu1-Cu2-P2	132.56(3)
P2-Cu2-Cl2	121.80(7)	Cu6-Cl5-Cu5	76.53(5)	Cl5-Cu6-Cl6	96.12(3)	P1-Ag1-Cl1	106.16(4)	Cu1-Cu2-O3	78.87(8)
P2-Cu2-Cl1	120.85(7)	Cu5-Cl6-Cu5	81.78(5)	Cl6-Cu6-Cl8	91.46(3)	P1-Ag1-P2	116.60(5)	Cu1-Cu2-O4	86.42(8)
P2-Cu2-Cl4	118.38(7)	Cu5-Cl6-Cu6	88.86(6)	P7-Cu7-Cl5	112.99(3)	P2-Ag1-Cl1	99.44(4)	Cu2-Cu1-P1	90.97(3)
Cl2-Cu2-Cl1	97.15(6)	Cu6-Cl6-Cu5	78.05(5)	P7-Cu7-Cl7	127.19(3)	P2-Ag1-Cl1	121.06(4)	Cu2-Cu1-O2	74.46(7)
Cl2-Cu2-Cl4	101.58(6)			P7-Cu7-Cl8	121.39(3)			Cu2-Cu1-O1	84.35(8)
Cl4-Cu2-Cl1	90.93(6)	**3-CuCl**		Cl5-Cu7-Cl7	93.35(3)	**3-AgCl**		P1-Cu1-O1	143.59(8)
P3-Cu3-Cl3	102.39(6)	P1-Cu1-Cl1	116.23(4)	Cl5-Cu7-Cl8	98.18(3)	P1-Ag1-Cl1	110.20(2)	P1-Cu1-O2	113.65(7)
P3-Cu3-Cl1	115.61(7)	P1-Cu1-Cl2	136.20(4)	Cl7-Cu7-Cl8	97.13(3)	Cl1-Ag1-Cl2	96.60(2)	P2-Cu2-O3	106.32(8)
P3-Cu3-Cl4	140.94(7)	P1-Cu1-Cl3	106.69(3)	P8-Cu8-Cl6	120.89(3)	Cl2-Ag1-P1	153.17(2)	P2-Cu2-O4	130.44(8)
Cl1-Cu3-Cl4	94.68(6)	Cl1-Cu1-Cl2	98.75(3)	P8-Cu8-Cl7	101.75(3)	P2-Ag2-Cl1	106.12(2)	O1-Cu1-O2	99.8(1)
Cl3-Cu3-Cl1	103.63(6)	Cl1-Cu1-Cl3	97.31(3)	P8-Cu8-Cl8	137.19(4)	P2-Ag2-Cl2	113.36(2)	O2-Cu1-O2	82.88(9)
Cl3-Cu3-Cl4	93.01(6)	Cl2-Cu1-Cl3	93.22(3)	Cl6-Cu8-Cl7	95.18(3)	P2-Ag2-Cl4	142.69(2)	O3-Cu2-O4	111.2(1)
P4-Cu4-Cl3	126.69(7)	P2-Cu2-Cl1	111.58(3)	Cl6-Cu8-Cl8	97.00(3)	Cl2-Ag2-Cl1	89.45(2)		
P4-Cu4-Cl2	110.41(6)	P2-Cu2-Cl2	123.87(4)	Cl7-Cu8-Cl8	93.11(3)	Cl4-Ag2-Cl1	101.07(2)	**3-AgOAc**	
P4-Cu4-Cl4	124.08(7)	P2-Cu2-Cl4	129.47(4)	Cu1-Cl1-Cu2	81.35(3)	Cl4-Ag2-Cl2	91.69(2)	Ag1-Ag2-P2	97.08(2)
Cl3-Cu4-Cl2	92.41(6)	Cl1-Cu2-Cl2	94.50(3)	Cu1-Cl1-Cu3	81.34(3)	P3-Ag3-Cl1	108.52(2)	Ag1-Ag2-O4	86.91(6)
Cl4-Cu4-Cl2	98.30(6)	Cl1-Cu2-Cl4	95.19(3)	Cu2-Cl1-Cu3	84.73(3)	P3-Ag3-Cl3	141.03(2)	Ag1-Ag2-O2	66.91(5)
Cl4-Cu4-Cl3	97.55(6)	Cl2-Cu2-Cl4	94.09(3)	Cu1-Cl2-Cu2	85.14(3)	P3-Ag3-Cl4	114.26(2)	Ag2-Ag1-O3	75.00(6)
P5-Cu5-Cl5	121.12(7)	P3-Cu3-Cl3	120.04(3)	Cu1-Cl2-Cu4	88.02(3)	Cl1-Ag3-Cl4	95.29(2)	Ag2-Ag1-O1	92.27(6)
P5-Cu5-Cl6	104.40(6)	P3-Cu3-Cl1	118.96(4)	Cu4-Cl2-Cu2	86.29(3)	Cl3-Ag3-Cl1	99.99(2)	Ag2-Ag1-P1	128.41(2)
Cl5-Cu5-Cl6	92.40(6)	P3-Cu3-Cl4	120.79(4)	Cu1-Cl3-Cu3	78.02(3)	Cl3-Ag3-Cl4	88.25(2)	P1-Ag1-O3	97.00(7)
Cl6-Cu5-Cl6	98.19(6)	Cl1-Cu3-Cl3	102.93(3)	Cu3-Cl3-Cu4	85.63(3)	P4-Ag4-Cl2	107.59(2)	P1-Ag1-O1	134.10(7)
P6-Cu6-Cl5	137.22(7)	Cl1-Cu3-Cl4	94.35(3)	Cu4-Cl3-Cu1	84.10(3)	P4-Ag4-Cl3	129.27(2)	O1-Ag1-O3	115.65(9)
P6-Cu6-Cl6	120.31(7)	Cl4-Cu3-Cl3	94.35(3)	Cu2-Cl4-Cu3	84.44(3)	P4-Ag4-Cl4	126.83(2)	P2-Ag2-O2	106.70(6)
Cl5-Cu6-Cl5	106.22(6)	P4-Cu4-Cl2	123.47(4)	Cu2-Cl4-Cu4	88.14(3)	Cl2-Ag4-Cl3	105.60(2)	P2-Ag2-O4	154.68(7)
Cl5-Cu6-Cl6	101.26(6)	P4-Cu4-Cl3	122.49(3)	Cu3-Cl4-Cu4	82.83(3)	Cl2-Ag4-Cl4	87.91(2)	O2-Ag2-O4	97.89(8)
Cu1-Cl1-Cu2	80.11(6)	P4-Cu4-Cl4	121.53(4)	Cu5-Cl5-Cu6	86.24(3)	Cl3-Ag4-Cl4	91.30(2)		
Cu2-Cl1-Cu3	85.13(6)	Cl2-Cu4-Cl4	91.28(3)	Cu5-Cl5-Cu7	83.21(3)	Ag1-Cl1-Ag3	90.38(2)	**2-AuCl**	
Cu3-Cl1-Cu1	77.49(5)	Cl3-Cu4-Cl4	96.59(3)	Cu6-Cl5-Cu7	82.87(3)	Ag1-Cl2-Ag2	88.42(2)	Cl1-Au1-P1	178.8(1)
Cu1-Cl2-Cu4	83.20(5)	Cl2-Cu4-Cl3	93.62(3)	Cu5-Cl6-Cu6	85.47(3)	Ag2-Cl1-Ag1	84.41(2)	Cl2-Au2-P2	177.6(1)
Cu1-Cl2-Cu2	81.18(6)	P5-Cu5-Cl5	118.80(3)	Cu5-Cl6-Cu8	83.61(3)	Ag2-Cl1-Ag3	80.93(2)		
Cu2-Cl2-Cu4	78.94(5)	P5-Cu5-Cl6	120.42(3)	Cu6-Cl6-Cu8	86.04(3)	Ag2-Cl4-Ag3	81.94(2)	**3-AuCl**	
Cu1-Cl3-Cu3	72.23(5)	P5-Cu5-Cl7	124.70(3)	Cu5-Cl7-Cu7	87.89(3)	Ag2-Cl2-Ag4	84.51(2)	Cl1-Au1-P1	176.92(9)
								Cl2-Au2-P2	178.02(9)

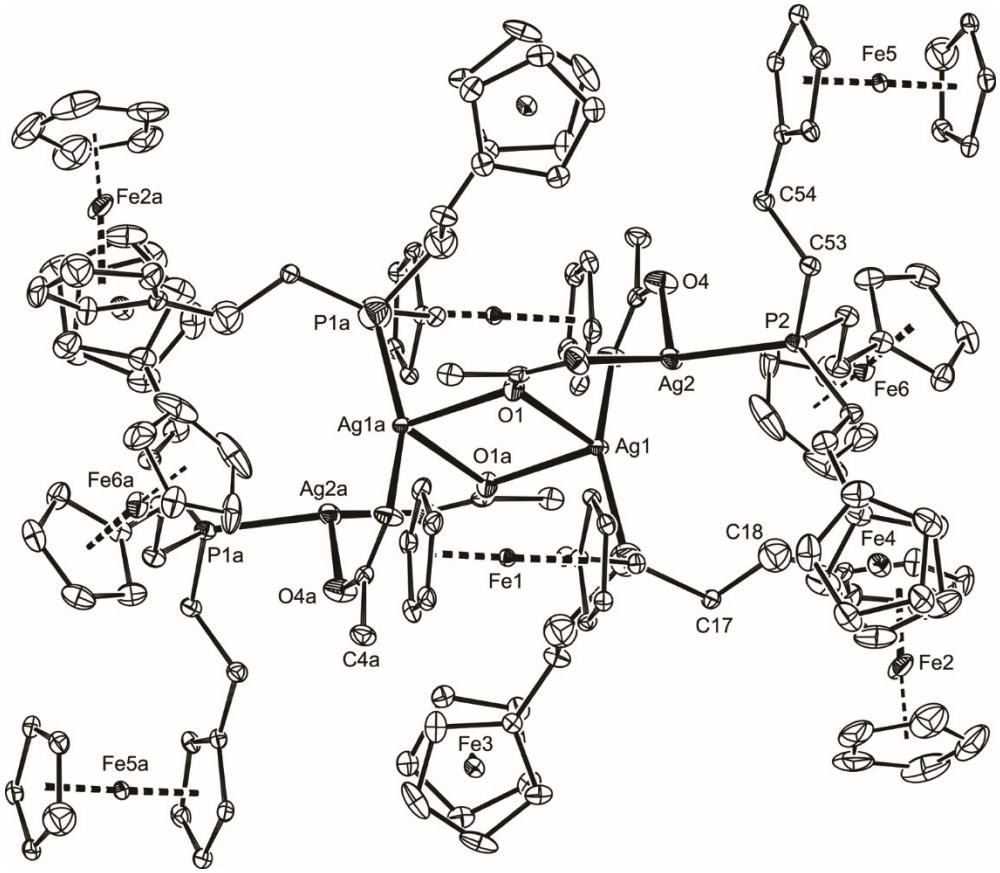

Figure S1. Thermal ellipsoid plot (40% probability level, hydrogen atoms are omitted for clarity) of **3-AgOAc**.

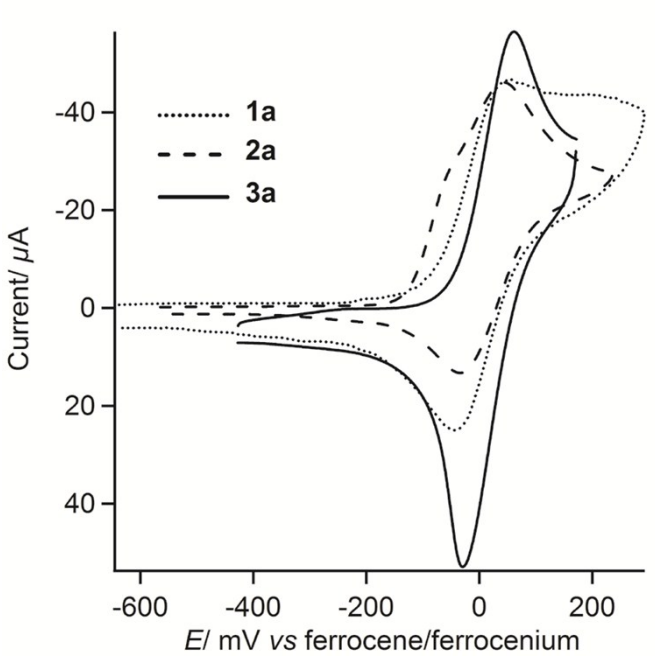

Figure S2. Cyclic voltammograms of a 1 mM solution of **1-CuCl**, **2-CuCl** and **3-CuCl** (scan rate 100 mVs^{-1}) (0.1 $mol.dm^{-3}$ of $^{n}Bu_4N[PF_6]$ in 2:1 DCM:acetonitrile) at 298 K.

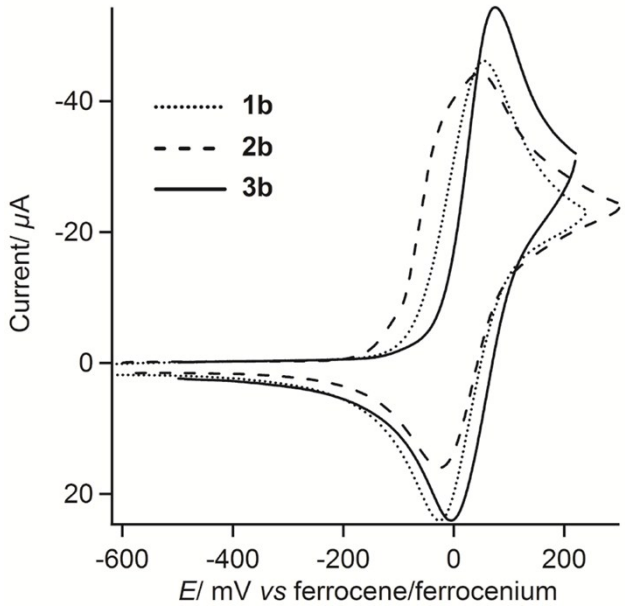

Figure S3. Cyclic voltammograms of a 1 mM solution of **1-AgCl**, **2-AgCl** and **3-AgCl** (scan rate 100 mVs^{-1}) (0.1 $mol.dm^{-3}$ of $^{n}Bu_4N[PF_6]$ in 2:1 DCM:acetonitrile) at 298 K.

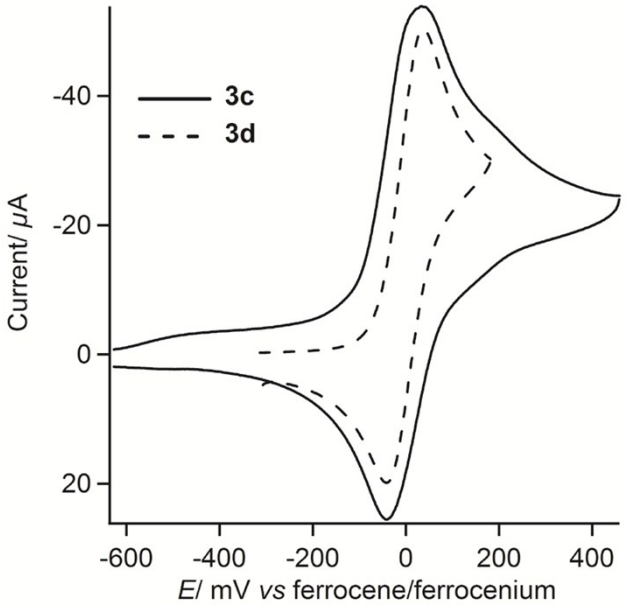

Figure S4. Cyclic voltammograms of a 1 mM solution of **3-CuOAc** and **3-AgOAc** (scan rate 100 mVs^{-1}) (0.1 $mol.dm^{-3}$ of $^{n}Bu_4N[PF_6]$ in 2:1 DCM:acetonitrile) at 298 K.

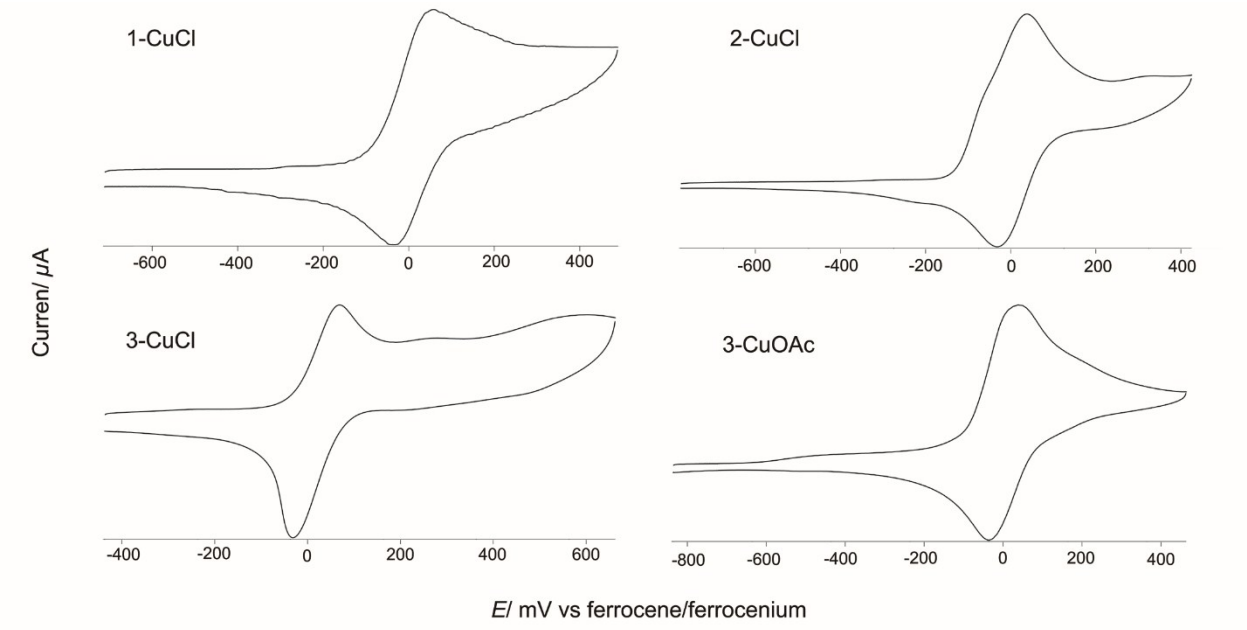

Figure S5. Cyclic voltammograms (wide scan) of 1 mM solutions of **1-CuCl**, **2-CuCl**, **3-CuCl** and 3-**CuOAc** (scan rate 100 mVs^{-1})(0.1 $mol.dm^{-3}$ of $^{n}Bu_4N[PF_6]$ in 2:1 DCM:acetonitrile) at 298 K.