Syntheses of Cu^{I} discrete polymetallic assemblies based on ligands bearing the 2,5-bis(2-pyridyl)phosphole fragment and Cu^{II} precursors

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Supporting information

General Procedures: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofurane, diethylether) or from phosphorus pentoxide (pentane, dichloromethane). All compounds were used as received without further purification. 1-phenyl-2,5-(2-pyridyl)phosphole **A**,[1] 1-phenyl-2,5-(2-pyridyl)thioxophosphole **1**,[2] and 1-phenyl-2,5-(2-pyridyl)oxophosphole **2**[2] were prepared as described in the literature. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300 or AM400. ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to $Si(CH_3)_4$ as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85 % H_3PO_4. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes1.

References for the General Procedure section :

1 : D. Le Vilain, C. Hay, V. Deborde, L. Toupet and R. Réau, *Chem. Commun*. **1999**, 345.
2 : C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, R. Réau, *Chem. Eur. J.*, **2001**, *7*, 4222.

S.1) Experimental section

1-phenyl-2,5-(2-pyridyl)selenoxophosphole 3 :

Red selenium (0.07 g, 0.804 mmol) was added upon stirring at room temperature to a solution of 1-phenyl-2,5-(2-pyridyl)phosphole **A** (0.30 g, 0,804 mmol) in THF (20 mL). After 24 hours, the solvents were removed in vacuum and the remaining solid was washed three times with 10 mL pentane. A yellow solid of 1-phenyl-2,5-(2-pyridyl)selenoxophosphole **3** was obtained (yield 74.5%, 268.0 mg, 0.67 mmol). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 1.73 (s, 4H, $C{=}CCH_2CH_2$), 3.04-3.26 (m, 4H, $C{=}CCH_2$), 7.01 (ddd, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 0.6 Hz, 2H, pyridyl H_5), 7.24-7.40 (m, 3H, phenyl H_{meta}, H_{para}), 7.48 (ddd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.0 Hz, 2H, pyridyl H_4), 7.59 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 0,6 Hz, 2H, pyridyl H_3), 7.78-7.89 (m, 2H, phenyl H_{ortho}), 8.45 (dd, ^3J(H,H) = 5.1 Hz, ^4J(H,H) = 1.0 Hz, 2H, pyridyl H_6). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 21.7 (s, $C{=}CCH_2CH_2$), 28.9 (d, ^3J(P,C) = 11.5 Hz, $C{=}CCH_2$), 121.3 (s, pyridyl C_5), 123.7 (d, ^3J(P,C) = 3.3 Hz, pyridyl C_3), 126.6 (d, ^1J(P,C) = 67.0 Hz, P-*C* or C_{ipso}), 127.9 (d, *J*(P,C) = 12.6 Hz, phenyl C_{meta} or C_{ortho}), 130,4 (d, *J*(P,C) = 12.1 Hz, phenyl C_{meta} or C_{ortho}), 131.0 (d, ^4J(P,C) = 3.3 Hz phenyl C_{para}), 132,1 (d, ^{1}(P,C) = 75.7 Hz, phenyl P-*C* or C_{ipso}), 134.9 (s, pyridyl C_4), 148.5 (d, ^4J(P,C)= 1.1 Hz, pyridyl C_6), 151.2 (d, ^2J(P,C) = 17.0 Hz, P-*C*=*C* or pyridyl C_2), 151.8 (d, ^2J(P,C) = 19.2 Hz, P-*C*=*C* or pyridyl C_2). ^{31}P NMR (121 MHz, CD_2Cl_2): δ = +40.4 (pseudo-triplet, ^1J(P,Se) = 366.8 Hz). HR-MS (EI) : $[M+]^+$ calcd for $C_{24}H_{21}N_2P_1Se_1$, 448.06076; found 448.0609; Anal. Calcd for $C_{24}H_{21}N_2P_1Se_1$: C, 64.43; H, 4.73; N, 6.26; Found C, 64.15; H, 4.49; N, 6.43.

Complex 4 :

A 100 mL schlenk flask was charged with 1-phenyl-2,5-(2-pyridyl)phosphole **A** (0.05 g, 0,136 mmol) in 10 mL of CH_2Cl_2. $Cu(OTf)_2$ (0.049 g, 0,136 mmol) was then added at room temperature leading to an immediate color change of the solution from yellow to dark green. After 10 minutes upon stearing at room temperature, the reaction mixture turned to light orange and stayed unchanged thereafter. After stirring the solution for one night, the solvents were removed under vacuum and the remaining solid was washed three times with 5 mL diethylether leaving an orange solid residue **4** (86 %yield, 68 mg, 0.117 mmol). Single crystals of **4** suitable for X-ray diffraction analyses were grown in one week from pentane vapor diffusion into a CH_2Cl_2 solution of the residue **4** (39 % yield, 31 mg, 0.053 mmol). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 1.84 (broad s, 4H, C=CCH$_2$C*H*$_2$), 2.03 (broad s, 4H, C=CCH$_2$C*H*$_2$), 2.86 (broad s, 4H, C=CC*H*$_2$), 3.20 (broad s, 4H, C=CC*H*$_2$), 7.05-7.72 (m, 18H, pyridyl $H_{3,4,5}$ phenyl H_{meta}, H_{para}), 7.83-8.41 (m, 4H, phenyl H_{ortho}), 8.44 (broad s, 4H, pyridyl H_6). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = 21.6 (broad s, CH_2), 27.9 (broad s, CH_2), 123.9 (broad s, CH), 130.0 (broad s, CH), 133.4 (broad s, CH), 139.8 (broad s, CH), 151.4 (broad s, CH). Quaternary carbons were not observed. ^{31}P NMR (121 MHz, CD_2Cl_2): δ = -3.5 (d, ^2J(P,P) = 94.2 Hz), +17.9 (d, ^2J(P,P) = 94.2 Hz). Anal. Calcd for $C_{52}H_{46}Cl_4Cu_2F_6N_4O_6P_2S_2$: C, 46.89; H, 3.48; N, 4.21; Found C, 46.55; H, 3.06; N, 4.33.

Complex 5 :

A 100 mL schlenk flask was charged with the ligand **1** (0.040 g, 0.1 mmol) in 10 mL of CH_2Cl_2. $Cu(OTf)_2$ (0.036 g, 0.1 mmol) was then added at room temperature leading to an immediate color of the solution from light yellow to dark red. After stirring the solution for 12 hours, the solvents were removed in vacuum and the remaining solid was washed three times with 10 mL of diethylether leaving a dark red solid residue **5** (91 % yield, 0.056 g, 0.015 mmol). Single crystals of **5a** and **5b** suitable for X-ray diffraction analyses were grown in one week from pentane vapor diffusion into a CH_2Cl_2 solution of the residue **5** (27 % yield, 0.017 g, 0.004 mmol). The yield was estimated considering that the molecular formula for **5** is $[Cu_6(\mathbf{1})_6]OTf_6$. Multinuclear MNR spectroscopy measurements were performed from the dark red solid residue **5** and confirmed by measurement performed on the batch of single crystals collected. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 1.89 (broad s, 24H, C=CCH$_2$C*H*$_2$), 2.75-3.20 (m, 24H, C=CC*H*$_2$), 7.22-7.70 (m, 42H, pyridyl H_5, phenyl H_{meta}, H_{para} and pyridyl H_4), 7.82 (broad s, 12H, phenyl H_{ortho}), 7.85-8.00 (m, 12H, pyridyl H_3), 8.45-8.85 (m, 12H, pyridyl H_6). ^{31}P-NMR (81 MHz, CD_2Cl_2): δ = +50.1 (broad s). Due to the very low solubility of the derivative **5** in CD_2Cl_2 and any common deuterated solvent, it was not possible to observe signal in the ^{13}C NMR spectrum. Anal. Calcd for $C_{153}H_{134}Cl_4Cu_7F_{21}N_{12}O_{23}P_6S_{13}$: C, 44.85; H, 3.30; N, 4.10; Found C, 45.03; H, 3.53; N, 4.47.

Complex 5' :

A 100 mL schlenk flask was charged with the ligand **1** (0.040 g, 0.1 mmol) in 10 mL of CH_2Cl_2. $Cu(BF_4)_2.xH_2O$ (0.025 g, 0.1 mmol) was then added at room temperature leading to a slow change in color of the solution from yellow to light green to dark green, and finally to dark orange. After stirring the solution for 3 hours, the solvents were removed in vacuum and the remaining solid was washed with 20 mL of diethyl ether leaving a dark orange solid of the derivative **5'** (90 % yield, 0.050 g, 0.015 mmol). The yield was estimated considering that the molecular formula for **5'** is $[Cu_6(\mathbf{1})_6](BF_4)_6$. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.61 (broad s, 12H, $C{=}CCH_2CH_2$), 1.82 (broad s, 12H, $C{=}CCH_2CH_2$), 2.62 (broad s, 12H, $C{=}CCH_2$), 2.92 (broad s, 12H, $C{=}CCH_2$), 7.32-7.42 (m, 30H, pyridyl H_5, phenyl H_{meta}, H_{para}), 7.59 (broad s, 12H, pyridyl H_4), 7.74 (broad s, 12H, phenyl H_{ortho}),7.97 (broad s, 12H, pyridyl H_3), 8.47 (broad s, 12H, pyridyl H_6). ^{31}P-NMR (162 MHz, CD_2Cl_2): δ = +49,4 (broad s). Due to the very low solubility of the derivative **5'** in CD_2Cl_2 and any common deuterated solvent, it was not possible to observe signal in the ^{13}C NMR spectrum. Anal. Calcd for $C_{150}H_{144}Cl_{12}Cu_6F_{24}B_6N_{12}P_6S_6$: C, 47.16; H, 3.80; N, 4.40; Found C, 46.73; H, 3.42; N, 4.67.

Complex 6 :

A 100 mL Schlenk flask was charged with the ligand **3** (0.045 mg, 0.1 mmol), $Cu(OTf)_2$ (0.036 mg, 0.1 mmol) and 10 mL of CH_2Cl_2. The solution immediately turned to a dark red colour. After stirring the solution for 12 hours, the solvents were removed in vacuum and the remaining solid was washed three times with 10 mL of diethylether leaving a dark red solid residue **6** (92 % yield, 0.061 mg, 0.012 mmol). Single crystals of **6a** and **6b** suitable for X-ray diffraction analyses were grown from pentane vapor diffusion into a CH_2Cl_2 solution of the residue **6** (19 % yield, 0.013 mg, 0.003 mmol). The yield was estimated considering that the molecular formula for **6** is $[Cu_6(\mathbf{3})_6]OTf_6$. Multinuclear MNR spectroscopy measurements were performed from the dark red solid residue **6** and confirmed by measurement performed on the batch of single crystals collected. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 1.51 (broad s, 12H, $C{=}CCH_2CH_2$), 1.81 (broad s, 12H, $C{=}CCH_2CH_2$), 2.46 (broad s, 12H, $C{=}CCH_2$), 2.96 (broad s, 12H, $C{=}CCH_2$), 7.09-7.72 (m, 54H, pyridyl $H_{3,4,5}$ phenyl H_{meta}, H_{para}), 8.00 (m, 12H, phenyl H_{ortho}), 8.45 (broad s, 12H, pyridyl H_6). ^{31}P NMR (121 MHz, CD_2Cl_2): δ = +34.4 (broad s). Due to the broadening of the ^{31}P NMR signal, it was not possible to observe the ^1J(P,Se) coupling constant. Due to the very low solubility of the derivative **6** in CD_2Cl_2 and any common deuterated solvent, it was not possible to observe signal in the ^{13}C NMR spectrum. Anal. Calcd for $C_{157}H_{138}Cl_{12}Cu_7F_{21}N_{12}O_{21}P_6S_7Se_6$: C, 40.27; H, 2.97; N, 3.59; Found C, 40.44; H, 3.08; N, 3.27.

S.2) X-ray Crystallographic Study :

Single crystals of **4**, **5a**, **5b**, **6a** and **6b** suitable for X-ray crystal analyses were obtained by slow diffusion of vapors of pentane into dichloromethane solutions. Single crystal data collection were performed at 100 K or at 150 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-*K*α radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[1] Structure determinations were performed by direct methods with the solving program SIR97,[2] that revealed all the non hydrogen atoms. SHELXL program[3] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters.

In the crystal lattices of the coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and to their counter-anions. These solvent molecules in most cases have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induce a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mount at low temperature (100 K or 150 K) as quickly as possible on the diffractometer gionometer and X-ray data collection were performed at low temperature (100 K or 150 K). In most of the case, X-ray crystal structure resolution revealed the counter-anions and solvent molecules highly disordered. In the case of the derivative **4** modelling of the disorder of the counter-anion and solvent molecules was possible leading to rather high anisotropic displacement parameters for some of their atoms. Nevertheless, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes are always satisfactory. This allows a primarily assignment of these modest R factor to an inadequate modelling of the disordered species exterior to the complex **4** and leads confidence to the treatment of the structural resolution of these derivatives. Table S1 gives the crystallographic data for this derivative **4**.

In the case of the derivative **5a**, disordered CH_2Cl_2 molecules occupy an important volume of the crystal cell and are found highly disorder. In addition, the triflate counter-anions as well as the $[Cu(H_2O)_4(OTf)_2]$ included complex were found also highly disorder. A modelling of these disorders was not possible and we have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules which cannot be satisfactory modelled. In this case, anisotropic displacement parameters associated to the atoms of the cationic coordination complex are satisfactory except for the C122 and C123 atoms that have been refined isotropically.

In the case of the derivative **5b**, disordered CH_2Cl_2 molecules occupy an important volume of the crystal cell and are found highly disorder. In addition, one triflate counter-anion was found also highly disorder. A modelling of these disorders was not possible and we have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules which cannot be satisfactory modelled. In this case, anisotropic displacement parameters associated to the atoms of the cationic coordination complex and the two remaining counter-anions are satisfactory, except for the C4 atom that have a high ADP max/min ratio responsible of a level A alert in the checkcif file. This is due to the fact that the fused cyclohexyl ring of one of the ligand **1** present in the derivative **5b** is disordered over two positions. Nevertheless all attempts performed in order to model this disorder have led to instable refinement cycles presumably due to a dominant relative distribution of one configuration over the other one.

In the case of the derivative **6a,** disordered CH_2Cl_2 molecules occupy an important volume of the crystal cell and are found highly disorder. A modelling of these disorders was not possible and we have proceeded to a ‘squeeze’ treatment in order to remove the scattering contribution of these molecules which can not be satisfactory modelled. In these cases, anisotropic displacement parameters associated to the atoms of the cationic coordination complex and their counter-anions are satisfactory.

In the case of the derivative **6b**, disordered CH_2Cl_2 and pentane molecules occupy an important volume of the crystal cell and are found highly disorder. In addition, triflate counter-anions was found also highly disorder. A modelling of these disorders was not possible and we have proceeded to a ‘squeeze’ treatment in order to remove the scattering contribution of these molecules which cannot be satisfactory modelled. In this case, anisotropic displacement parameters associated to the atoms of the cationic coordination complex are satisfactory except for the C1, C20, C31, C70 and N12 atoms that have been refined isotropically.

Table S1 gives the crystallographic data for the derivatives **5a**, **5b**, **6a** and **6b** after this ‘squeeze’ treatment. Table S2 gives the crystallographic data for the derivatives **5a**, **5b**, **6a** and **6b** before such ‘squeeze’ treatment.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[4] CCDC reference numbers 927129, 927130, 927131, 927133 and 927132 contain the supplementary crystallographic data for derivatives **4**, **5a**, **5b**, **6a** and **6b** respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data

Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

References for the X-ray crystallography section :

1 Otwinowski, Z.; Minor, W. In *Methods in Enzymology*, (Ed.: C.W. Carter, Jr. & R.M. Sweet), New York:Academic Press**,** 1997, *276*, 307.

2 Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.G.G., Polidori, G.; Spagna, R. *J. of Applied Cryst.* **1999**, *32*, 115.

3 Sheldrick G.M., *SHELX97,* Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

4 International Tables for X-ray Crystallography, vol C, Ed. Kluwer, Dordrech, 1992.

Table S1 . Crystal data and structure refinement for **4**, **5a**, **5b**, **6a** and **6b**

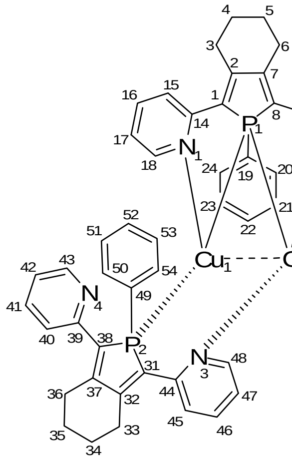
	4	**5b**	**5a**
Molecular formula	$C_{53}\ H_{48}\ C_{l6}\ Cu_2\ F_6\ N_4\ O_6\ P_2\ S_2$	$C_{148}\ H_{126}\ C_{l0}\ Cu_6\ F_{12}\ N_{12}\ O_{12}\ P_6\ S_{10}$	$C_{144}\ H_{126}\ C_{l0}\ Cu_6\ F_0\ N_{12}\ O_0\ P_6\ S_6$
CCDC number	927129	927131	927130
Molecular weight	1416.79	3380.27	2783.99
a (Å)	14.724(4)	14.961(1)	16.956(2)
b (Å)	14.984(4)	18.271(2)	18.436(3)
c (Å)	26.752(7)	19.021(2)	19.618(2)
α (°)	90	118.348 (3)	109.285(2)
β (°)	98.041(2)	104.380(3)	102.617(3)
γ (°)	90	101.818(2)	113.337(2)
V (Å^3)	5844(3)	4103(2)	4864(2)
Z	4	1	1
Dc (g cm^{-3})	1.610	1.368	0.950
Crystal system	monoclinic	triclinic	triclinic
Space group	P21/n	P-1	P-1
Temperature (K)	150(2)	150(2)	100(2)
Wavelength Mo-$K\alpha$ (Å)	0.71069	0.71069	0.71069
Crystal size (mm)	0.18*0.13*0.09	0.18*0.11*0.06	0.12*0.08*0.05
μ (mm^{-1})	1.200	1.021	0.796
F(000)	2872	1726	1434
θ limit (°)	2.56 – 20.76	1.27 - 26.42	1.20 - 26.41
Index ranges hkl	$-15\leq h\leq 18$,	$-18\leq h\leq 18$,	$-20\leq h\leq 21$,
	$-16\leq k\leq 18$,	$-22\leq k\leq 22$,	$-23\leq k\leq 23$,
	$-33\leq l\leq 31$	$-23\leq l\leq 18$	$-24\leq l\leq 14$
Reflections collected	38234	23008	34019
Independant reflections	11632	16408	19288
Reflections [I>2σ(I)]	6223	10042	8036
Data/restraints/parameters	11632 / 0 / 730	16408 / 0 / 929	19288 / 0 / 775
Goodness-of-fit on F^2	1.018	0.945	0.809
Final R indices [I>2σ(I)]	$R1$= 0.0791	$R1$= 0.0657	$R1$= 0.0659
	$wR2$= 0.1883	$wR2$= 0.1720	$wR2$= 0.1668
R indices (all data)	$R1$= 0.1670	$R1$= 0.1023	$R1$= 0.1301
	$wR2$= 0.2366	$wR2$= 0.1908	$wR2$= 0.1864
Largest diff peak and hole (e Å^{-3})	0.781and -0.922	0.063 and -0.709	1.445 and -0.631

	6b	**6a**
Molecular formula	C_{144} H_{126} C_{l0} Cu_6 F_0 N_{12} O_0 P_6 S_0 Se_6	C_{154} H_{126} C_{l0} Cu_8 F_{30} N_{12} O_{40} P_6 S_{10} Se_6
CCDC number	927132	927133
Molecular weight	3065.39	4843.17
a (Å)	17.136(3)	16.945(1)
b (Å)	33.131(6)	18.478(1)
c (Å)	17.782(9)	20.154(2)
α (°)	90	107.916(2)
β (°)	107.947(9)	104.980(2)
γ (°)	90	112.985(2)
V (Å^3)	9604(5)	4984.7(7)
Z	2	1
Dc (g cm^{-3})	1.060	1.613
Crystal system	monoclinic	triclinic
Space group	P21/c	P-1
Temperature (K)	150(2)	150(2)
Wavelength Mo-*K*α (Å)	0.71069	0.71069
Crystal size (mm)	0.12*0.09*0.02	0.24*0.16*0.08
μ (mm^{-1})	1.878	2.183
F(000)	3084	2410
θ limit (°)	1.23 – 27.50	1.18 – 27.56
Index ranges *hkl*	$-17 \le h \le 22$,	$-22 \le h \le 21$,
	$-42 \le k \le 39$,	$-22 \le k \le 24$,
	$-22\le l \le 22$	$-24\le l \le 26$
Reflections collected	51706	46121
Independant reflections	21602	22033
Reflections [I>2$\sigma(I)$]	7148	13554
Data/restraints/parameters	21602 / 0 / 759	22033 / 0 / 1205
Goodness-of-fit on F^2	0.782	1.004
Final *R* indices [I>2$\sigma(I)$]	$R1$= 0.0768	$R1$= 0.0591
	$wR2$= 0.1595	$wR2$= 0.1535
R indices (all data)	$R1$= 0.1880	$R1$= 0.1005
	$wR2$= 0.1834	$wR2$= 0.1710
Largest diff peak and hole (e Å^{-3})	1.235 and -0.667	1.223 and -1.128

Table S2 . Crystal data and structure refinement for **5a**, **5b**, **6a** and **6b** before the 'squeeze' treatment

	5a	**5b**	**6a**	**6b**
Molecular formula	$C_{79} H_{67} Cl_4 Cu_4 F_{15} N_6 O_{22} P_3 S_8$	$C_{154} H_{130} Cl_8 Cu_6 F_{16} N_{12} O_{16} P_6 S_{12}$	$C_{160} H_{138} Cl_{12} Cu_8 F_{30} N_{12} O_{42} P_6 S_{10} Se_6$	$C_{84} H_{83} Cl_8 Cu_3 F_9 N_6 O_9 P_3 S_3 Se_3$
Molecular weight	2482.74	3944.08	5384.72	2391.75
a (Å)	16.956(5)	14.961(1)	16.945(5)	17.136(3)
b (Å)	18.436(5)	18.271(1)	18.478(5)	33.131(6)
c (Å)	19.618(5)	19.021(2)	20.154(5)	17.782(9)
α (°)	109.285(5)	118.348(2)	107.916(5)	90.000(5)
β (°)	102.617(5)	104.380(3)	104.980(5)	107.947(9)
γ (°)	113.337(5)	101.818(2)	112.985(5)	90.000(5)
V (Å^3)	4864(2)	4103(2)	4985(2)	9604(4)
Z	2	1	1	4
Dc (g cm^{-3})	1.695	1.596	1.794	1.654
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	P21/c
Temperature (K)	100(2)	150 (2)	293(2)	293(2)
Wavelength Mo-$K\alpha$ (Å)	0.71069	0.71069	0.71069	0.71069
Crystal size (mm)	0.12*0.08*0.05	0.18*0.11*0.06	0.24*0.16*0.08	0.12*0.09*0.02
μ (mm^{-1})	1.294	1.189	2.349	2.208
F(000)	2502	2002	2678	4800
θ limit (°)	1.20 – 26.41	1.27 – 26.42	1.18 – 27.56	1.23 – 27.50
Index ranges *hkl*	$-20 \le h \le 21$, $-23 \le k \le 23$, $-24\le l \le 14$	$-18 \le h \le 18$, $-22 \le k \le 22$, $-23\le l \le 18$	$-22 \le h \le 21$, $-22 \le k \le 24$, $-24\le l \le 26$	$-17 \le h \le 22$, $-42 \le k \le 39$, $-22\le l \le 22$
Reflections collected	34019	23008	46257	51754
Independant reflections	19288	16408	22072	21615
Reflections [I>2σ(I)]	9094	10341	13851	7862
Data/restraints/parameters	19288 / 0 / 1200	16408 / 0 / 1064	22072 / 0 / 1271	21615 / 0 / 1147
Goodness-of-fit on F^2	1.225	1.080	1.053	0.974
Final R indices [I>2σ(I)]	R1= 0.1281 wR2= 0.3387	R1= 0.0865 wR2= 0.2210	R1= 0.0620 wR2= 0.1727	R1= 0.1032 wR2= 0.2251
R indices (all data)	R1= 0.2335 wR2= 0.4130	R1= 0.1372 wR2= 0.2711	R1= 0.1168 wR2= 0.2186	R1= 0.2697 wR2= 0.3032
Largest diff peak and hole (e Å^{-3})	3.838 and -1.903	-2.537 and 2.442	1.850 and -1.714	1.292 and -1.098

Scheme S1. Labelling scheme adopted for the atoms of the ligands **A** in the complex **4**



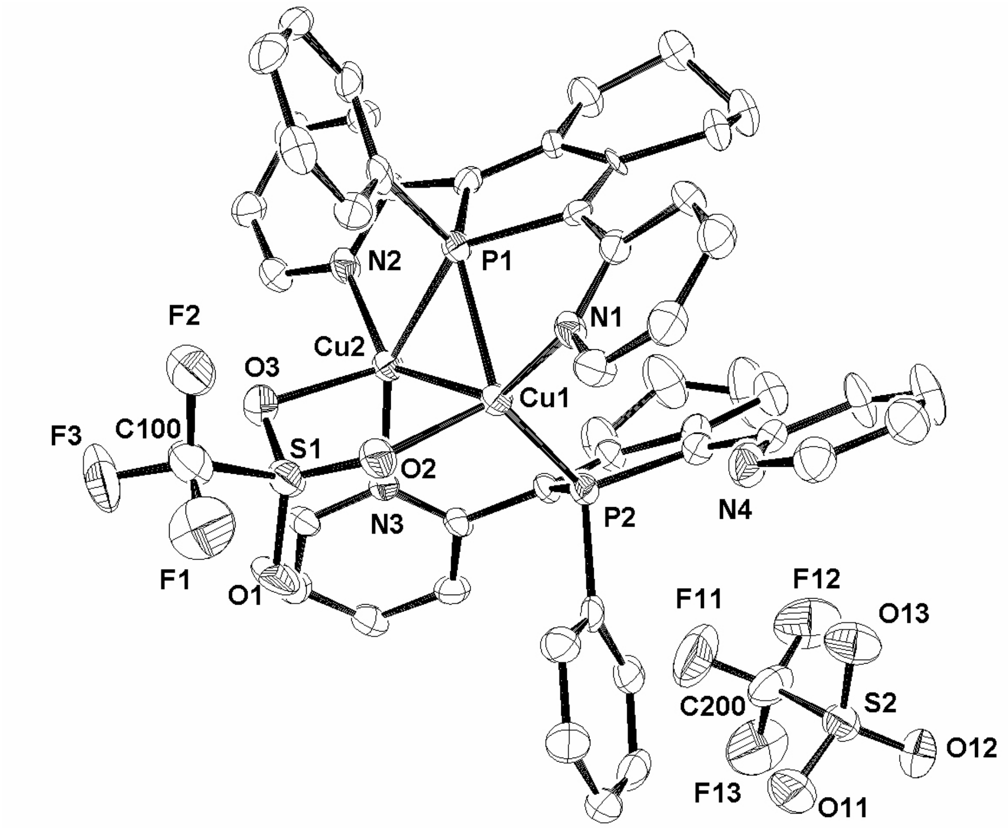
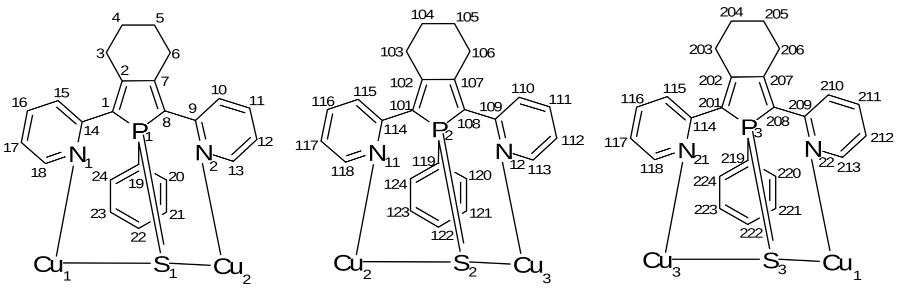


Figure S1. Molecular structure of the complex **4** (thermal ellipsoids 50% probability). Hydrogen atoms and included solvent CH_2Cl_2 molecules have been omitted for clarity.

Scheme S2. Labelling scheme adopted for the atoms of the ligands **1** in the complex **5a**



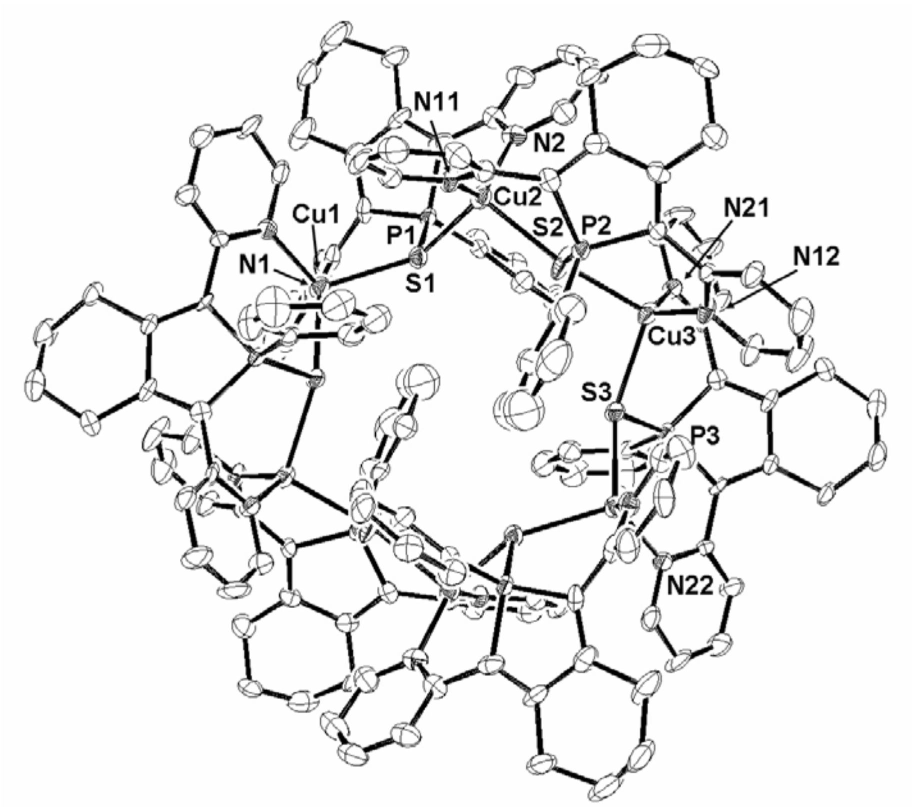
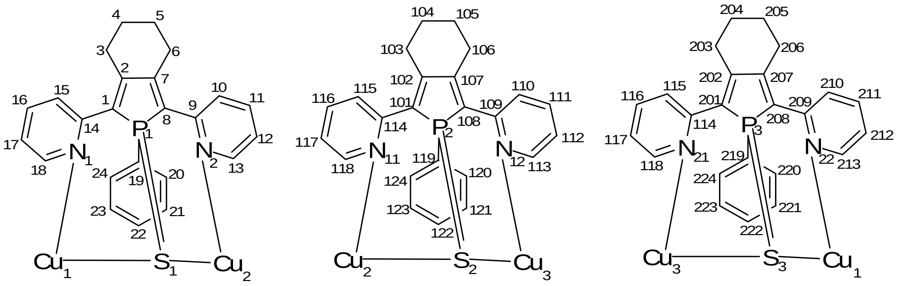


Figure S2. Molecular structure of the complex **5a** (thermal ellipsoids 50% probability). Hydrogen atoms, OTf- counter-anions, included $[Cu(H_2O)_4(OTf)_2]$ complexes and included solvent molecules have been omitted for clarity.

Scheme S3. Labelling scheme adopted for the atoms of the ligands **1** in the complex **5b**



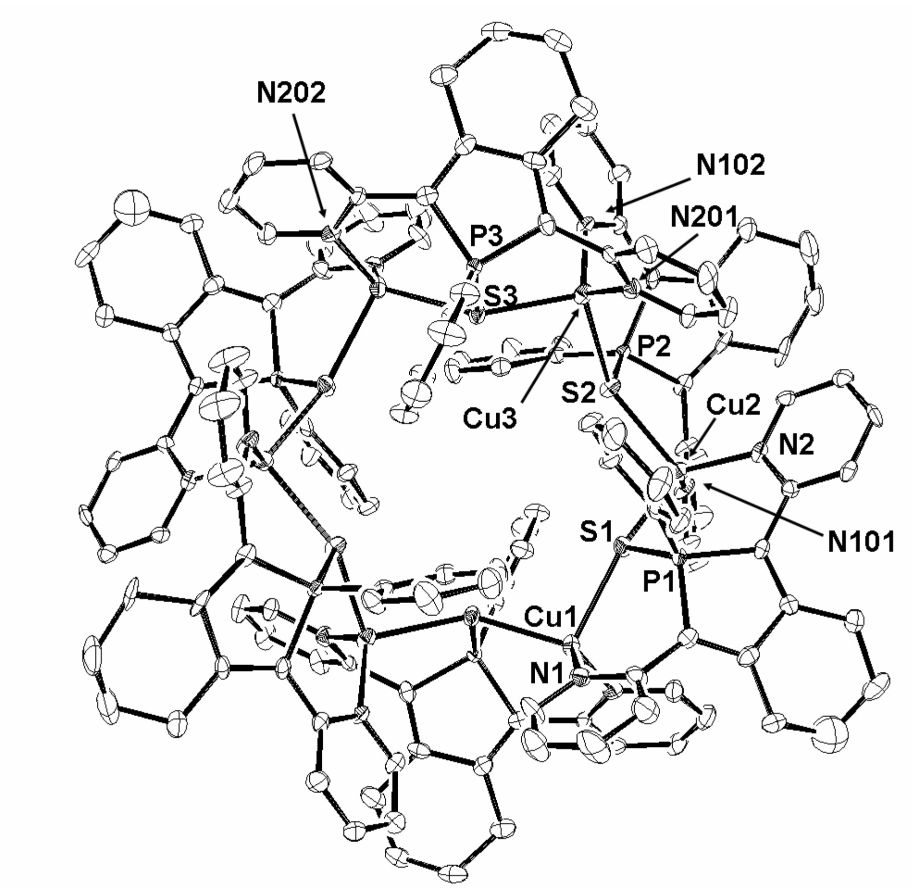
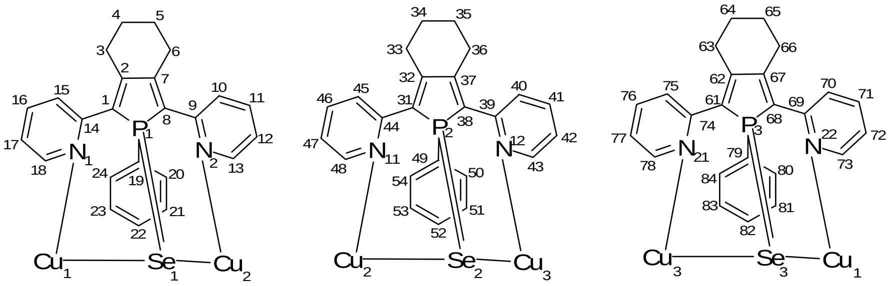


Figure S3. Molecular structure of the complex **5b** (thermal ellipsoids 50% probability). Hydrogen atoms, OTf- counter-anions, included [Cu(H_2O)$_4$(OTf)$_2$] complexes and included solvent molecules have been omitted for clarity.

Scheme S4. Labelling scheme adopted for the atoms of the ligands **3** in the complex **6a**



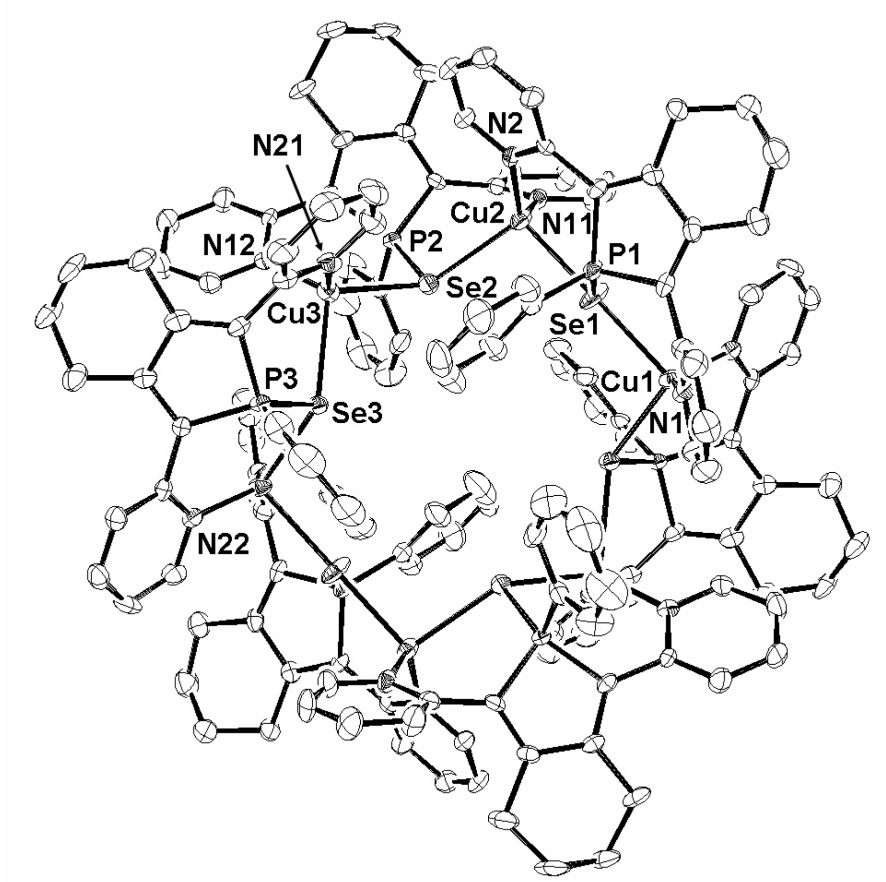
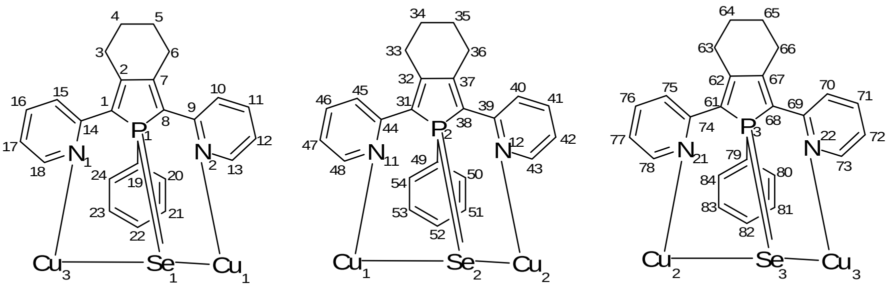


Figure S4. Molecular structure of the complex **6a** (thermal ellipsoids 50% probability). Hydrogen atoms, OTf- counter-anions and included solvent molecules have been omitted for clarity.

Scheme S5. Labelling scheme adopted for the atoms of the ligands **3** in the complex **6b**



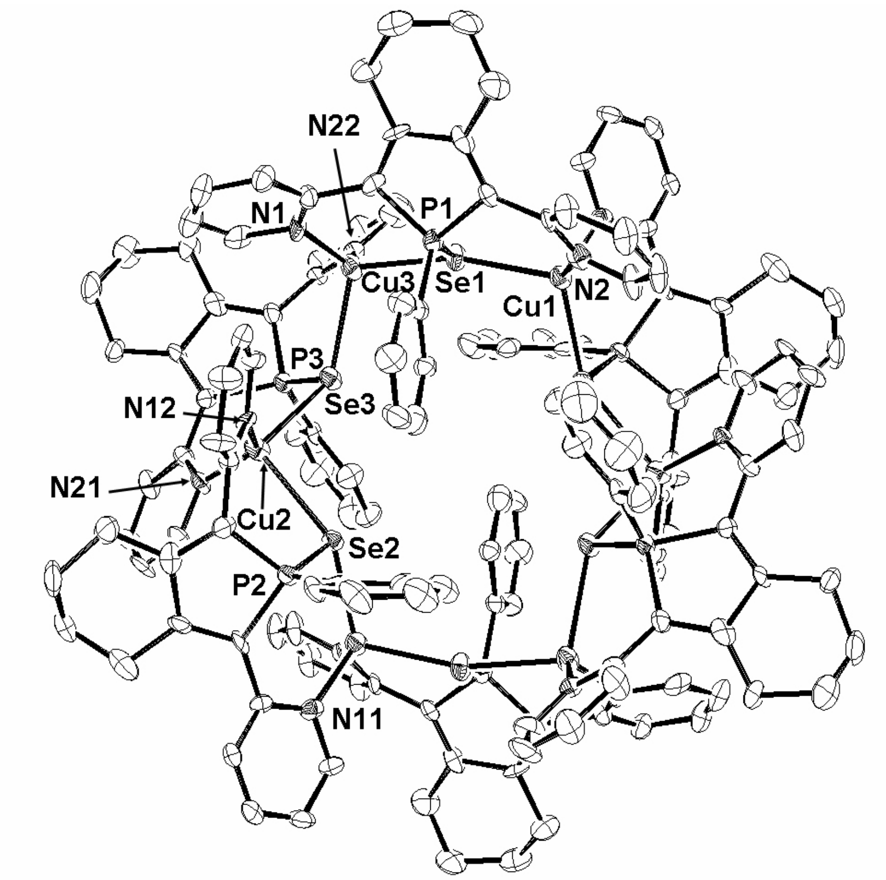


Figure S5. Molecular structure of the complex **6b** (thermal ellipsoids 50% probability). Hydrogen atoms, OTf- counter-anions and included solvent molecules have been omitted for clarity.

S.3) Preliminary characterization of a tricationic monometallic complex:

Along our attempts to grow single crystals from the derivative **5**, in one case a solution of the derivative **5** left for several months under pentane vapors diffusion in inert atmosphere afforded, in addition to the batch of red single crystal of **5a** and **5b,** a very few amount of tiny yellow single crystals of the derivative **S5**. Despite dimensions of these crystals were very small and the diffraction pattern quality low, it was possible to establish the molecular structure of this derivative due to x-ray diffraction studies on single crystal (table S3, data given for a crystal structure resolution treatment without any squeeze treatment; the highest residual electronic densities are located at the vicinity of disordered CH_2Cl_2 solvant molecules).

According to this x-ray diffraction crystal structure analysis, derivative **S5** is a tricationic monometallic complex (Fig S6) featuring two bis(2-pyridyl)-2-thioxophospholene ligands S**1** (Fig. S7) that coordinate a distorted tetrahedral metal center acting as S,N chelate. Three non-coordinated OTf^- counter-anion are present in the asymmetric unit together with four CH_2Cl_2 solvent molecules. Two particular structural points deserve to be discussed concerning this structure:

1) The tetrahedral geometry about the C(8) and C(38) carbon atoms this is in accordance with a sp^3-hybridisation for these two carbon atoms. The endocyclic P-C distances are characteristic for single bonds [1.795(8)- 1.865(8) Å], while the C(1)-C(2) [1.336(11) Å]; C(31)-C(32) [1.361(11) Å] and C(7)-C(8) [1.518(10) Å]; C(37)-C(38) [1.526(11) Å] bond distances are typical for double and a single C-C bonds, respectively. These solid state parameters are clearly consistent with a bis(2-pyridyl)-2-thiophospholene derivative. Conversely, the short C(6)-C(7) [1.342(11) Å] and C(36)-C(37) [1.328(11) Å] separation and the planar geometry at C(6) and C(36) clearly show that the fused carbocycle is a cyclohexene fragment. Therefore, an isomerization of the phosphole ring of the ligand **1** occurred along this crystallization experiment affording the derivative **S5**. Note that the two ligands present in the coordination sphere of the metal centers are the diastereoisomer that have the H-atom residing on the C(8) or C(38) atoms and the P-substituent in mutual *cis*-configuration.

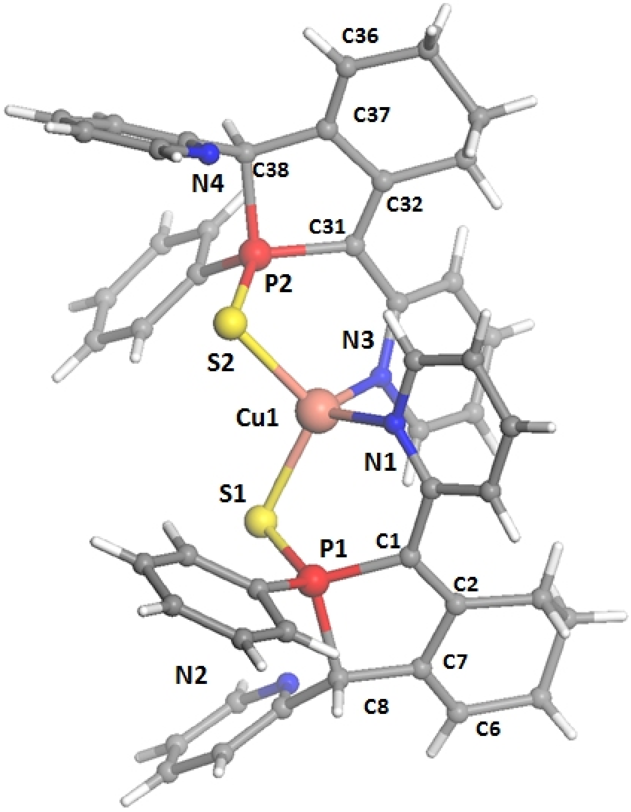


Figure S6. Molecular structure of the complex **S5** . OTf- counter-anions and included solvent molecules have been omitted for clarity.

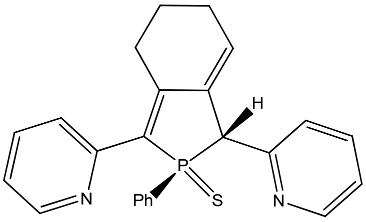


Figure S7. Structure of the ligand **S1**.

Isomerization of a phosphole ring of the ligand **A** to a 2-thiophospholene ring induced by the coordination of the ligand onto metal centers (Pd^{II} and Pt^{II} metal centers) was previously observed.[1] In addition, it was also demonstrated that, in a general extend, oxidation of the P-atom of slightly aromatic σ^3-phospholes affords σ^4-derivatives exhibiting a small antiaromatic character.[2] Although this switch in aromatic-antiaromatic stabilization is small, it can destabilizes σ^4-phosphole derivatives with respect to their phospholene isomers. Therefore, the characterization of a complex of a bis(2-pyridyl)-2-thiophospholene ligand is not very surprising, especially considering the fact that this isomerization process, accompanied with a very low yield, has been very slow.

2) The complex **S5** is a a tricationic monometallic complex. Cu^{III} coordination complexes have been scarcely described[3] and one can question if the species **S5** is correctly formulated as a Cu^{III}complex or Cu^{II} species bearing one oxidized ligand. Additionally, one could also

consider a Cu^{II} species bearing one of the two free pyridine moieties protonated. Nevertheless, investigation of the metric parameters observed in this solid state structure does not allow observing any striking differences between the two ligands **S1** present in the coordination sphere of the metal centers. Note also that the light yellow color of the crystals does not particularly support the possibility of a Cu^{II} complex that is usually highly colored. On the other hand, a distorted tetrahedral coordination sphere is quite unlikely for a Cu^{III} metal center. Therefore, at that stage of our investigations, one cannot exclude any of these hypotheses to describe this tricationic monometallic complex based on a copper ion.

This complex **S5** might be an indirect proof of the occurrence, along the reaction of this ligand with the Cu(OTf)$_2$ salt, of a redox process centered on a transient Cu^{II} complex that could be the electron source explaining the formation of the Cu^{I} complexes described in this work. Note again that this reaction seemingly occurred very slowly with a very low yield and we have not been enough to collect enough materials to date to perform any spectroscopic characterization. In addition, to date, we have not been able to reproduce the crystallization of the derivative **S5**. **Therefore these results and hypotheses should be considered with a lot of caution** at this stage of our studies.

References for the section S3:

1 a) Leca, F.; Sauthier, M.; le Guennic, B.; Lescop, C.; Toupet, L.; Halet, J-F.; Réau, R. *Chem. Commun,* **2003**, 1774; b) Leca, F.; Lescop, C.; Toupet, L.; Réau , R. *Organometallics*, **2004**, *23*, 6191.

2 Nyulaszi, L.; Holloczki, O.; Lescop, C.; Hissler, M.; Réau, R. *Organic & Biomolecular Chemistry*, **2006**, *4(6)*, 996

3 a) Hanss, J.; Krüger H-J. *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 2827; b) Krebs, C.; Glaster, T.; Bill, E.; Weyhermüller, T. Meyer-Klauche, W.; Wieghart, K. *Angew. Chem. Int. Ed. Engl.*, **1999**, *38*, 359; c) Jos, B.C.; Sanz, J.L.; Ibanez, M.J.; Vila, G.; Lloret, F.; Julve, M.; Ruiz, R.; Ottenwaelder, X.; Aukauloo, A.; Poussereau, S.; Journaux, Y.; Carmen Munoz, M.; *J. Chem. Soc., Dalton Trans.*, **1998**, 781; c) Yao, B.; Wang, D-X.: Huang, Z-T.; Wang, M-X. *Chem. Commun.*, **2009**, 2899; d) Garcia-Lopez, J.; Yanez-Rodriguez, V.; Roces, L.; Garcia-Granda, S.; Martinez, A.; Guevara-Garcia, A.; Castro, G.R.; Jimenez-Villacorta, F.; Iglesias, M.I.; Lopez Ortis, F. *J. Am. Chem. Soc.*, **2010**,*132*, 10665.

Table S3 . Crystal data and structure refinement for **SA**

	SA . 3OTf, 4 CH_2Cl_2
Molecular formula	$C_{55}H_{47}Cl_8Cu_4F_9N_6O_9P_2S_5$
CCDC Number	934187
Molecular weight	1648.35
a (Å)	15.993(2)
b (Å)	26.367(3)
c (Å)	32.189(3)
α (°)	90
β (°)	90
γ (°)	90

V (Å^3)	13574(5)
Z	8
Dc (g cm^{-3})	1.613
Crystal system	orthorhombic
Space group	Pnaa
Temperature (K)	150(2)
Wavelength Mo-$K\alpha$ (Å)	0.71069
Crystal size (mm)	0.15*0.05*0.02
μ (mm^{-1})	0.918
F(000)	6664
θ limit (°)	1.00 – 26.45
Index ranges *hkl*	$-19 \leq h \leq 16$, $-33 \leq k \leq 26$, $-39 \leq l \leq 38$
Reflections collected	51614
Independant reflections	13773
Reflections [$I > 2\sigma(I)$]	8270
Data/restraints/parameters	13773 / 0 / 857
Goodness-of-fit on F^2	1.111
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1098$ $wR2 = 0.2273$
R indices (all data)	$R1 = 0.1770$ wR2= 0.2576
Largest diff peak and hole (e Å^{-3})	2.803 and -1.501