The coordination behavior of 2,3-bis(diphenylphosphino)maleic-N-phenylimide towards copper, silver, gold and palladium

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Electronic supplementary data

Syntheses and characterization

All syntheses were carried out under an atmosphere of nitrogen using standard Schlenk technique. Elemental analyses were carried out by an "elementar vario MICRO cube". Infrared spectra were recorded by a "Perkin Elmer spectrum GX" spectrometer; UV-vis absorption spectra were recorded on a "Perkin Elmer Lambda 900" spectrometer.

Synthesis of 2,3-bis(diphenylphosphino)maleic-N-phenylimide (L1)

Synthesis for cyclic imide

Dichloromaleic anhydride (1.2 eq) was added to a solution of aniline in acetic acid and stirred under reflux for at least 6h. After cooling to room temperature the pale yellow precipitate was filtered, washed with cyclohexane for several times and dried under vacuum.

Synthesis of **L1**

$Ph_2PSi(CH_3)_3$ (5.74 mL, 22 mmol) in 10mL cyclohexane was added to the suspension of cyclic imide (2.42 g, 10 mmol) in 30 mL cyclohexane dropwise at 0 ˚C. The mixture was stirred at room temperature for 14 h. The orange precipitate was filtered, washed with cyclohexane for several times and then dried under vacuum. Yield= 4.95 g (9.1 mmol, 91 %) ^{31}P NMR: -23.36. IR (KBr, cm^{-1}): 1767(w), 1711(s), 1596(w), 1520(w), 1500(w), 1484(w), 1455(w), 1434(m), 1367(s), 1188(m), 1109(m), 1094(m), 1068(w), 741(s), 692(s), 633(w).

Synthesis of [CuL1L1˙] (1)

10 mL toluene were added to a mixture of **L1** (108 mg, 0.2 mmol) and CuOAc (13 mg, 0.1 mmol). After stirring at room temperature for one hour the suspension was heated to reflux for 30 min. While cooling to room temperature [Cu**L1L1˙**] (**1**) crystalizes as dark reddish orange plates as **1**·2toluene (**1a**) and **1**·toluene (**1b**). Yield= 48 mg (0.042 mmol, 84 %). Anal. Calcd for $C_{68}H_{50}N_2O_4P_4Cu$: C, 71.23; H, 4.40; N, 2.44.Found: C, 72.32; H, 4.64; N, 2.33. IR (KBr, cm^{-1}): 1770 (w), 1717(s), 1664(m), 1641(w), 1610(s), 1499(m), 1482(m), 1454(w), 1434(m), 1363(s), 1338(s), 1241 (w), 1186(w), 1095(m), 1068(w), 1025(w), 998(w), 843(w), 816(w), 736(s), 690(s), 629(w), 617(w), 576(w), 539(w), 503(s), 475(m), 436(w).

Synthesis of $[(CuOAc)_4(L1)_2]$ (2)

A solution of **L1** (468 mg, 0.866 mmol) in 10 mL DCM was added to a solution of CuOAc(157 mg, 1.276 mmol) in 10 mL DCM yielding a dark violet reaction mixture immediately. The solution was transferred to Schlenk tube and layered with cyclohexane. $[(CuOAc)_4(\mathbf{L1})_2]$ (**2**) crystallizes simultaneously blueish violet crystals of two shapes: plates (**2a**) and blocks (**2b**). Yield= 382 mg (0.24 mmol, 75%) ^{31}P NMR: -19.86. Anal. Calcd for $C_{76}H_{62}N_2O_{12}P_4Cu_4$: C, 58.02; H, 3.97; N, 1.78. Found: C, 56.92; H, 4.12; N, 1.78. IR (KBr, cm^{-1}): 1767 (w), 1713(s), 1563(s), 1518(w), 1499(w), 1486(w), 1433(s), 1418(s), 1370(s), 1263(w), 1189(w), 1168(w), 1111(m), 1096(m), 1071(w), 1047(w), 1026(w), 1000(w), 986(w), 815(w), 765(w), 741(s), 727(m), 690(s), 672(m), 635(w), 617(w), 495(m), 470(m), 420(w).

Synthesis of $[Cu_2Br_2(L1)_2]$ (3)

A solution of **L1** (108 mg, 0.2 mmol) in 4 mL DCM was added to a suspension of CuBr (14 mg, 0.1 mmol) in 3 mL DCM resulting in a brown solution. After 2.5h the solution was transferred into a Schlenk tube and layered with cyclohexane. $[Cu_2Br_2(\mathbf{L1})_2]$ (**3**) was obtained brownish blue block crystals after two days. Yield= 42 mg (0.031 mmol, 62 %). ^{31}P NMR: 25.34. Anal. Calcd for $C_{68}H_{50}N_2O_4P_4Cu_2Br_2$: C, 59.62; H, 3.68; N, 2.04. Found: C, 59.92; H, 4.12; N, 1.78. IR (KBr, cm^{-1}): 1769 (w), 1716(s), 1597(w), 1556(w), 1502(m), 1484(w), 1435(m), 1366(s), 1262(w), 1189(m), 1095(m), 1065(w), 1027(w), 998(w), 906(w), 815(w), 763(w), 738(s), 688(s), 631(w), 577(w), 506(w), 480(s), 461(m), 431(w).

Synthesis of $[Cu_2I_2(L1)_2]$ (4)

A solution of **L1** (108 mg, 0.2 mmol) in 5 mL DCM was added to a suspension of CuI (19 mg, 0.1 mmol) in 3 mL DCM resulting in a brown solution. After 2.5h the solution was transferred into a Schlenk tube and layered with cyclohexane. $[Cu_2I_2(\mathbf{L1})_2]$ (**4**) was obtained as bluish grey block crystals after two days. Yield= 44 mg (0.03 mmol, 59 %). ^{31}P NMR: -28.65. Anal. Calcd for $C_{68}H_{50}N_2O_4P_4Cu_2I_2$: C, 55.79; H, 3.44; N, 1.91. Found: C, 55.68; H, 3.44; N, 1.98. IR (KBr, cm^{-1}): 1769 (w), 1716(s), 1597(w), 1556(w), 1502(m), 1484(w), 1435(m), 1367(s), 1262(w), 1189(m), 1110(m), 1094(m), 1065(w), 1026(w), 997(w), 815(w), 763(w), 737(s), 687(s), 631(w), 578(w), 505(w), 480(s), 460(m), 431(w).

Synthesis of $[Cu(L1)_2](SO_4)$ (5)

A solution of **L1** (76 mg, 0.14 mmol) in 4 mL DCM was added to a suspension of water-free $CuSO_4$ (12 mg, 0.07 mmol) in 3 mL DCM. After stirring for 14 h the reaction mixture was filtered and the filtrate was layered with *n*-heptane. [Cu $(\mathbf{L1})_2](SO_4)$ (**5**) was obtained as brownish red block crystals. Yield= 48 mg (0.04 mmol, 56 %). ^{31}P NMR: 1.55. Anal. Calcd for $C_{68}H_{50}N_2O_8P_4CuS$: C, 65.73; H, 4.06; N, 2.25; S, 2.58. Found: C, 59.23; H, 4.08; N, 2.07;S, 2.28. IR (KBr, cm^{-1}): 1775 (w), 1719(s), 1597(w), 1502(m), 1483(m), 1456(w), 1435(s), 1375(s), 1313(w), 1256(m), 1219(m), 1190(m), 1112(m), 1095(m), 1068(w), 1021(m), 1006(m), 913(m), 822(w), 737(s), 689(s), 634(w), 618(w), 574(w), 505,496(m), 479(m), 460(w), 430(w), 416(w).

Synthesis of [Cu(L1L2')] (6)

10 mL toluene were added to a mixture of **L1** (108 mg, 0.2 mmol) and copper acetat (13 mg, 0.1 mmol) and stirred for two hours leading to a clear brown solution. **L2** (24 mg, 0.05 mmol) dissolved in 2 ml toluene are added and the mixture is heated to reflux for 30 min. While cooling to room temperature a brownish red precipitate and a few very tiny, dark orange crystals of **6** suitable for single crystal X-Ray analysis are formed.

Synthesis of [AgL1L1'] (7)

10 mL toluene were added to a mixture of **L1** (117 mg, 0.217 mmol) and silver cyclohexylthiolate (24 mg, 0.108 mmol). After stirring at room temperature for half an hour the suspension was heated to reflux for 30 min. While cooling to room temperature [Ag**L1L1'**] (**7**) crystalizes simultaneously as dark red cubes (**7a**) and plates (**7b**). Yield= 87 mg (0.073 mmol, 68 %) Anal. Calcd for $C_{68}H_{50}N_2O_4P_4Ag$: C, 68.58; H, 4.23; N, 2.35.Found: C, 68.55; H, 4.44; N, 2.31. IR (KBr, cm^{-1}): 1766 (w), 1712(s), 1658(s), 1607(s), 1495(m), 1481(m), 1453(w), 1434(m), 1333(s), 1263 (w), 1232(w), 1173(w), 1094(m), 1024(w), 1000(w),912(w), 816,803(w), 737(s), 690(s), 624(w), 569(w),506(m), 477(m), 456(w).

Synthesis of [Ag(L1)$_2$](NO$_3$) (8)

A solution of **L1** (108 mg,0.2 mmol) in 5 mL toluene was added to a suspension of $AgNO_3$ (17 mg, 0.1 mmol) in 5 mL toluene and the mixture was stirred for 14 h. The precipitate was filtered, washed several times with toluene and dried under vacuum. The orange solid was redissolved in 5 mL DCM and layered with *n*-heptane. [Ag(**L1**)$_2$](NO$_3$) (**8**) crystallizes as orange plates within several days. Yield= 61 mg (0.049 mmol, 49 %). ^{31}P NMR: -4.61(d), -5.85(d). Anal. Calcd for $C_{68}H_{50}N_3O_7P_4Ag$: C, 65.19; H, 4.02; N, 3.35.Found: C, 62.29; H, 3.98; N, 3.23. IR (KBr, cm^{-1}): 1773 (w), 1716(s), 1596(w), 1501(m), 1482(m), 1435(m), 1364(s), 1186(m), 1094(m), 1068(w), 1025(w), 999 (m), 914(w), 821(w), 741(s), 690(s),634(w), 616(w), 579(w), 500(m), 477(m), 461(m), 436(w).

Synthesis of [Au(L1)$_2$]Cl (9)

A solution of **L1** (108 mg, 0.2 mmol) in 5 mL DCM was added to a solution of AuCl(tht) (32 mg, 0.1 mmol; tht = tetrahydrothiophene) in 5 mL DCM giving a violet reaction mixture. After stirring at room temperature for 0.5 h the mixture was filtered. Layering the filtrate with toluene results in red, bar-like crystals of **9a**, layering with leads to also red and bar-like crystals of **9b**. Yield (**9b**) = 93 mg (0.071 mml, 71 %). ^{31}P NMR: 15.47. Anal. Calcd for $C_{68}H_{50}N_2O_4P_4AuCl$: C, 62.09; H, 3.83; N, 2.13. Found: C, 62.21; H, 3.88; N, 2.22. IR (KBr, cm^{-1}): 1773 (w), 1716(s), 1598(w), 1501(m), 1484(w), 1435(s), 1375(s), 1313(w),1261(w), 1189(m), 1095(s), 1025(w), 1004(w), 919(w), 820, 802(w), 739(s), 690(s), 634(w), 617(w), 583(w), 498(m), 481(m), 438(w), 420(w).

Synthesis of [Au(L1)$_2$](PF$_6$) (10)

A solution of **L1** (108 mg, 0.2 mmol) in 8 mL DCM was added to a mixture of AuCl(tht) (32 mg, 0.1 mmol) and KPF_6(37 mg, 0.2 mmol) in 8 mL DCM yielding a purple reaction mixture. After stirring at room temperature for 2.5 hours the suspension was filtered and the filtrate was layered with *n*-heptane. [Au(**L1**)$_2$](PF$_6$) (**10**) was obtained as bluish violet, bar-like crystals within several days. Yield= 90 mg (0.063 mmol, 63 %). ^{31}P NMR: 15.50. Anal. Calcd for $C_{68}H_{50}F_6N_2O_4P_5Au$: C, 57.32; H, 3.54; N, 1.97. Found: C, 57.09; H, 4.05; N, 2.08. IR (KBr, cm^{-1}): 1775 (w), 1719(s), 1598(w), 1501(m), 1483(m), 1436(s), 1373(s), 1315(w), 1189(m), 1112(m), 1095(m), 1070(w), 1026(w), 1004(w), 839(s), 766(w), 739(s), 690(s), 633(w), 557(m), 496(m), 479(m).

Synthesis of [Pd(L1')$_2$] (11)

A solution of **L1** (468 mg,0.866 mmol)in 10 mL DCM was added to the solution of Pd(PPh$_3$)$_4$ (500 mg, 0.433 mmol) in 10 mL DCM. After stirring at room temperature for 15 minutes the solution was transferred into a Schlenk tube and layered with cyclohexane. Within two days [Pd(**L1'**)$_2$] (**11**) was obtained simultaneously in to modes: as dark redish brown block-like crystals (**11a**) and dark red blocks (**11b**). Yield= 427 mg (0.36 mmol, 83 %). Anal. Calcd for $C_{68}H_{50}N_2O_4P_4Pd$: C, 68.66; H, 4.24; N, 2.36.Found: C, 69.02; H, 4.14; N, 2.27. IR (KBr, cm^{-1}): 1717(m), 1670(s), 1618(s), 1493(m), 1480(m), 1434(m), 1360(w), 1337(s), 1263(w), 1240(s), 1179(w), 1095(m), 1054(w), 1023(w), 732(s), 685(s), 583(s), 506(s), 477(s).

Synthesis of [PdCl$_2$(L1)] (12)

A solution of **L1** (234 mg, 0.433 mmol)in 5 mL DCM was added to a suspension of PdCl$_2$(PPh$_3$)$_2$ (152 mg, 0.216 mmol) in 5 mL DCM yielding a clear solution. After stirring for half an hour the solution was transferred into a Schlenk tube and layered with *n*-heptane. After several days [PdCl$_2$(**L1**)] (**12**) crystallized simultaneously in three different modes: as yellow, hexagonal blocks (**12a**), as yellow to orange needles (**12b**) and as light yellow needles (**12c**). Yield= 121 mg (0.17 mmol, 79 %). Anal. Calcd for $C_{34}H_{25}Cl_2NO_2P_2Pd$: C, 56.81; H, 3.51; N, 1.95.Found: C, 56.28; H, 3.53; N, 1.93. IR (KBr, cm^{-1}):1774 (w), 1719(s), 1592(w), 1494(m), 1436(s), 1356(s), 1261(w), 1187(s), 1099(s), 1067(m), 1012(w), 845(w), 803(w), 746,734(s), 687(s),630,617(w), 593(w), 534(w), 508(s), 484,476(s), 451(m), 415(w).

Synthesis of [Pd(L1)$_2$](PF$_6$)$_2$ (13)

A solution of **L1** (54 mg,0.1 mmol) in 2 mL DCM was added to a mixture of PdCl$_2$(PPh$_3$)$_2$ (35 mg, 0.05 mmol) and KPF_6 (19 mg, 0.1 mmol) in 2 mL DCM. After stirring at room temperature for four hours the mixture was filtered. The solid was extracted with hot acetone from this solution **13a** crystallizes within several days as a small amount of light yellow blocks. From the original DCM-filtrate **13b** crystallizes within two days as large orange plates. Yield (from **13b**) = 41 mg (0.028 mmol, 56 %). Anal. Calcd for $C_{68}H_{50}F_{12}N_2O_4P_6Pd$: C, 55.21; H, 3.41; N, 1.89.Found: C, 55.31; H, 3.36; N, 1.95. IR (KBr, cm^{-1}): 1777 (w), 1725(s), 1587(w), 1494(w), 1439(m), 1369(s), 1191(m), 1173(w), 1098(s), 1072(w), 1012(w), 834(s), 771(w), 738(s), 689(s), 557(m), 502(m), 481(m).

UV-vis absorption spectra

L1

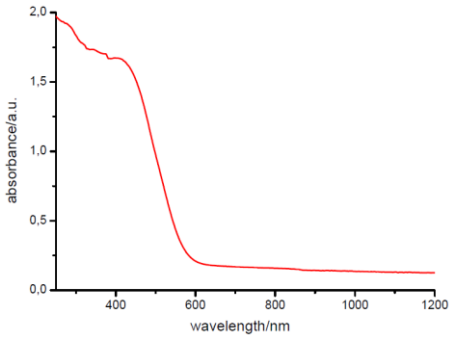

Figure S1: absorption spectrum of **L1**.

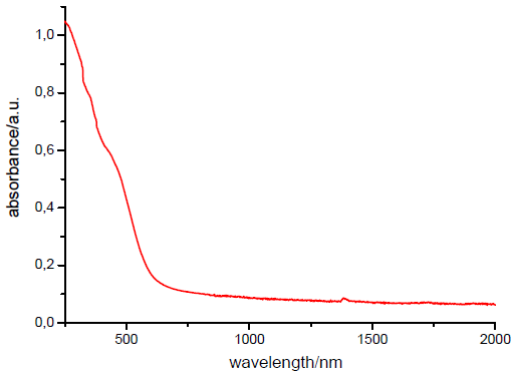

Figure S2: absorption spectrum of **1**.

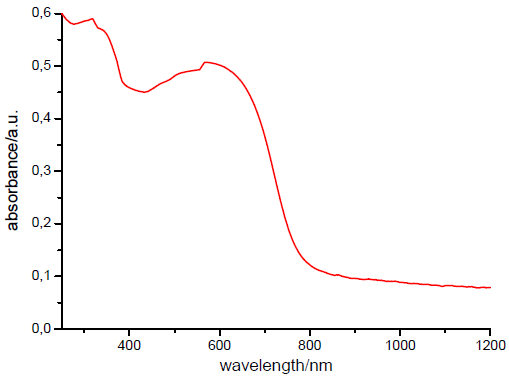

Figure S3: absorption spectrum of **2**.

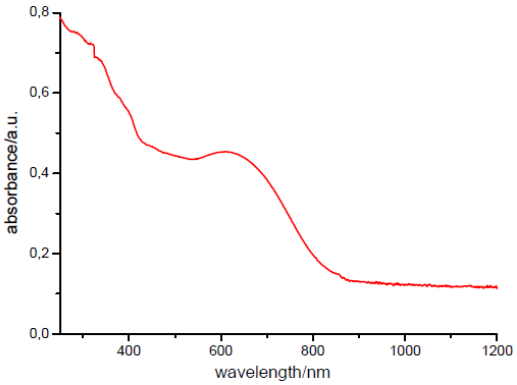

Figure S4: absorption spectrum of **3**.

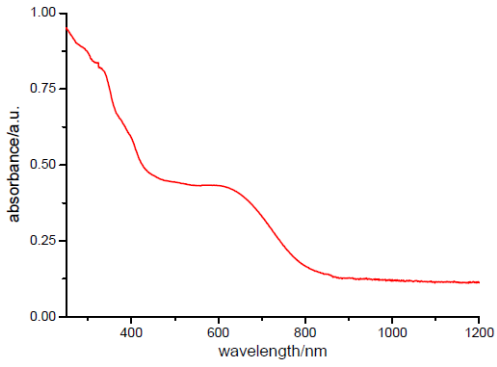

Figure S5: absorption spectrum of **4**.

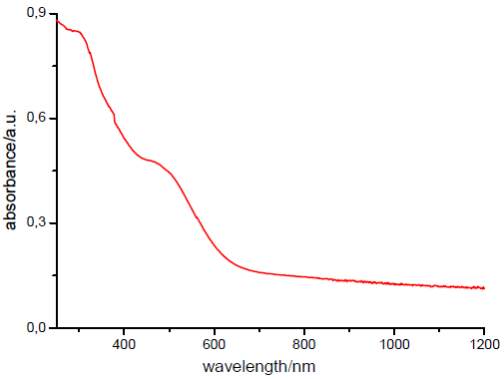

Figure S6: absorption spectrum of **5**.

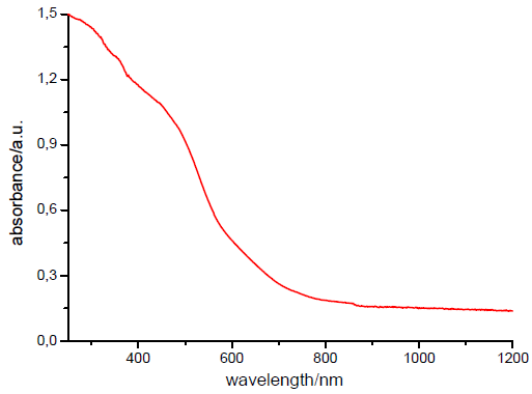

Figure S7: absorption spectrum of **7**.

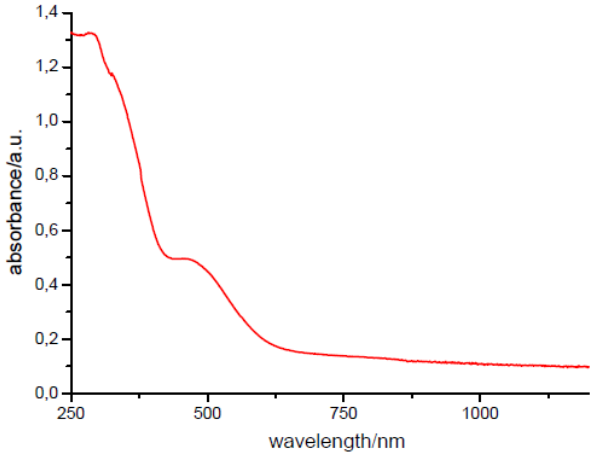

Figure S8: absorption spectrum of **8**.

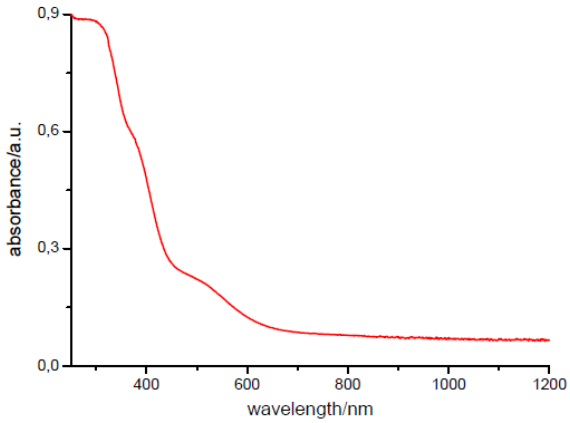

Figure S9: absorption spectrum of **9**.

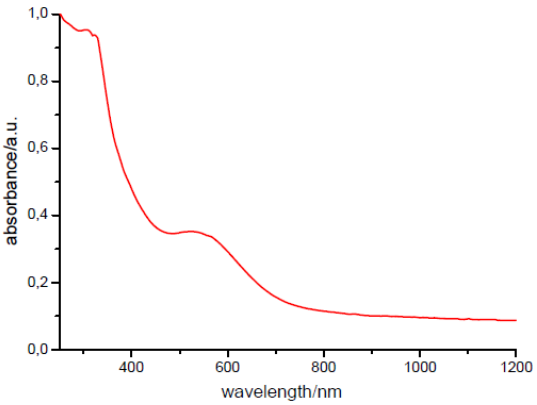

Figure S10: absorption spectrum of **10**.

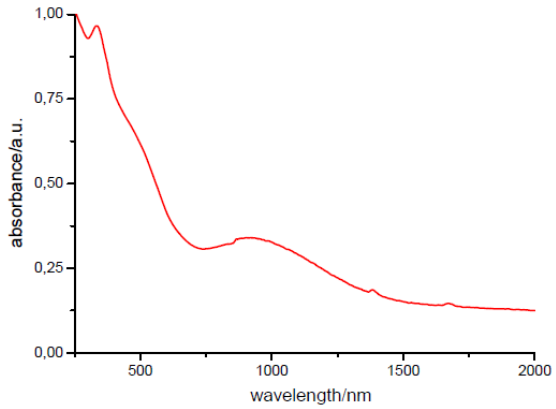

Figure S11: absorption spectrum of **11**.

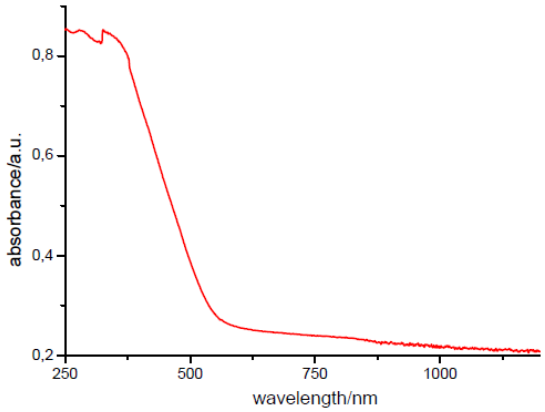

Figure S12: absorption spectrum of **12**.

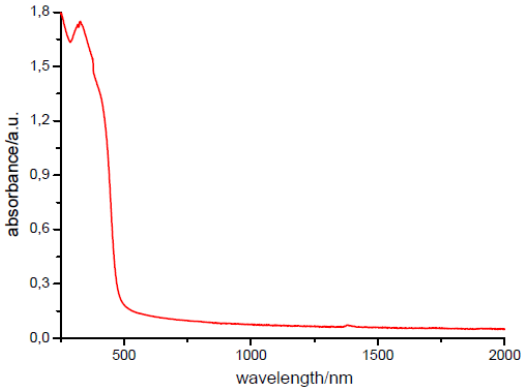

Figure S13: absorption spectrum of **13**.

Single crystal X-ray analyses

The structures of all crystalline products **L1** and **1**–**13** were determined by single crystal X-ray analysis. Suitable crystals were selected and investigated on a *Stoe StadiVari* or *Stoe IPDS2T* diffractometer using either Cu-Kα (λ = 1.54186 Å) or Mo-Kα (λ = 0.71073 Å) radiation. The crystals were kept at low temperature during data collection. Using Olex2 [1], the structures were solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. Non-hydrogen atoms were refined with anisotropic displacement parameters (disordered atoms were refined isotropically); hydrogen atoms were modelled on idealized positions. Crystallographic and refinement data of **L1** and **1**–**13** are summarized in Table S1.

CCDC-1847908 (**L1**) and 1847913–1847934 (**1a**–**13b**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Table S1: Crystallographic and refinement data of **L1** and **1**–**13**.

Comp.	**L1**	**1**·2tol (**1a**)	**1**·tol (**1b**)	**2**·DCM·½cyhex (**2a**)	**2**·2DCM (**2b**)	**3**	**4**	**5**·2¼DCM·¾H_2O
Emp. formula	$C_{34}H_{25}NO_2P_2$	$C_{82}H_{66}CuN_2O_4P_4$	$C_{75}H_{58}CuN_2O_4P_4$	$C_{80}H_{70}Cl_2Cu_4N_2O_{12}P_4$	$C_{78}H_{66}Cl_4Cu_4N_2O_{12}P_4$	$C_{68}H_{50}Br_2Cu_2N_2O_4P_4$	$C_{68}H_{50}Cu_2I_2N_2O_4P_4$	$C_{70.25}H_{56}Cl_{4.5}CuN_2O_{8.75}P_4S$
Molar mass	541.49	1330.78	1238.65	1700.32	1743.16	1369.88	1463.86	1446.67
Temperature/K	180.15	150.15	180.15	193.15	193.15	180.15	180.15	170.15
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1$	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.1405(5)	15.3583(12)	11.2383(5)	11.6182(3)	11.6227(3)	9.6363(5)	9.7400(4)	12.8008(3)
b/Å	14.1299(8)	16.3686(13)	15.6851(7)	27.1979(10)	12.3603(3)	10.6489(6)	10.7051(5)	13.2596(3)
c/Å	17.4630(7)	26.495(2)	17.5534(10)	12.3853(3)	27.4728(7)	14.9290(8)	14.8603(7)	22.2280(5)
α/°	90	90	84.797(4)	90	97.427(2)	79.104(4)	80.278(4)	93.294(2)
β/°	91.071(3)	90	79.338(4)	104.088(2)	91.569(2)	73.427(4)	73.675(4)	105.141(2)
γ/°	90	90	84.311(4)	90	103.892(2)	85.740(4)	86.021(4)	109.829(2)
Volume/$Å^3$	2748.4(2)	6660.7(10)	3017.5(3)	3795.9(2)	3792.16(17)	1441.50(14)	1465.23(12)	3381.32(14)
Z	4	4	2	2	2	1	1	2
ρ_{calc}g/cm^3	1.309	1.327	1.363	1.488	1.527	1.578	1.659	1.421
μ/mm^{-1}	0.191	1.800	0.523	1.323	1.394	2.288	1.941	3.750
F(000)	1128.0	2772.0	1286.0	1740.0	1776.0	692.0	728.0	1485.0
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54186)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54186)
2Θ range /°	3.66–52.0	6.65–127.4	4.35–53.7	2.99–54.2	3.54–54.0	4.41–58.4	4.36–58.5	7.18–120.0
Refl. collected	12386	21146	25887	47051	67389	16180	15162	20010
Independent refl.	5310 [R_{int} = 0.0276, R_σ = 0.0387]	10422 [R_{int} = 0.0679, R_σ = 0.0773]	12702 [R_{int} = 0.0432, R_σ = 0.0701]	16526 [R_{int} = 0.0389, R_σ = 0.0488]	31716 [R_{int} = 0.0472, R_σ = 0.0464]	7711 [R_{int} = 0.0299, R_σ = 0.0382]	7755 [R_{int} = 0.0413, R_σ = 0.0615]	9587 [R_{int} = 0.0259, R_σ = 0.0212]
Ind. refl. I ≥ 2σ(I)	4030	7679	8370	13476	28263	6036	5694	8630
Data/rest./param.	5310/0/352	10422/1/840	12702/14/770	16526/17/936	31716/3/1882	7711/0/370	7755/0/370	9587/5/824
Gof	1.053	1.017	0.975	1.009	1.073	0.956	0.941	1.029
R indexes [I ≥ 2σ(I)]	R_1 = 0.0383 wR_2 = 0.0919	R_1 = 0.0531 wR_2 = 0.1201	R_1 = 0.0536 wR_2 = 0.1252	R_1 = 0.0402 wR_2 = 0.0909	R_1 = 0.0623 wR_2 = 0.1691	R_1 = 0.0275 wR_2 = 0.0603	R_1 = 0.0344 wR_2 = 0.0680	R_1 = 0.0647 wR_2 = 0.1715
R indexes [all data]	R_1 = 0.0570 wR_2 = 0.0974	R_1 = 0.0858 wR_2 = 0.1358	R_1 = 0.0915 wR_2 = 0.1387	R_1 = 0.0577 wR_2 = 0.0982	R_1 = 0.0695 wR_2 = 0.1759	R_1 = 0.0440 wR_2 = 0.0646	R_1 = 0.0612 wR_2 = 0.0745	R_1 = 0.0702 wR_2 = 0.1754
Diff. peak/hole /e$Å^{-3}$	0.34/–0.23	0.44/–0.29	0.85/–0.46	0.96/–0.45	0.84/–0.78	0.39/–0.48	0.61/–0.68	2.25/–1.02
Flack parameter	–	0.03(2)	–	0.435(12)	0.130(11)	–	–	–
CCDC no.	1847908	1847913	1847914	1847915	1847916	1847917	1847918	1847919

Table S1 (continued)

Comp.	**6**·xDCM	**7a**	**7**·tol (**7b**)	**8**·1½DCM	**9**·2tol (**9a**)	**9**·3DCM (**9b**)	**10**·2½DCM (**10a**)	**10**·2½DCM (**10b**)
Emp. formula	$C_{69}H_{53}CuNO_5P_4$	$C_{68}H_{50}AgN_2O_4P_4$	$C_{75}H_{58}AgN_2O_4P_4$	$C_{69.5}H_{53}AgCl_3N_3O_7P_4$	$C_{82}H_{66}AuClN_2O_4P_4$	$C_{71}H_{56}AuCl_7N_2O_4P_4$	$C_{70.5}H_{55}AuCl_5F_6N_2O_4P_5$	$C_{70.5}H_{55}AuCl_5F_6N_2O_4P_5$
Molar mass	1163.54	1190.85	1282.98	1380.25	1499.66	1570.17	1637.23	1637.23
Temperature/K	180.15	180.15	180.15	150.15	180.15	180.15	180.15	180.15
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P1$	Pc	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	26.7644(7)	15.5703(6)	14.3361(5)	17.7091(4)	11.6909(4)	42.9195(12)	13.3647(4)	13.3809(3)
b/Å	34.3227(7)	16.7709(5)	15.8794(6)	11.3716(2)	15.5366(5)	11.5745(2)	14.5914(7)	28.6900(6)
c/Å	25.9458(7)	21.7141(8)	21.5123(7)	31.5245(7)	20.1956(7)	29.7098(8)	19.3008(8)	19.3683(5)
α/°	90	90	78.636(3)	90	75.302(3)	90	95.619(3)	90
β/°	118.490(2)	106.686(3)	74.660(3)	93.761(2)	74.805(3)	113.822(2)	108.526(3)	108.168(2)
γ/°	90	90	83.840(3)	90	89.165(3)	90	97.034(3)	90
Volume/$Å^3$	20948.1(10)	5431.4(3)	4622.3(3)	6334.8(2)	3418.9(2)	13501.6(6)	3504.3(3)	7064.8(3)
Z	12	4	3	4	2	8	2	4
$\rho_{calc}g/cm^3$	1.107	1.456	1.383	1.447	1.457	1.545	1.552	1.539
μ/mm^{-1}	1.657	0.544	0.485	5.138	5.712	2.602	2.469	2.450
F(000)	7236.0	2444.0	1983.0	2820.0	1520.0	6288.0	1634.0	3268.0
Radiation	CuKα (λ = 1.54186)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54186)	CuKα (λ = 1.54186)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range /°	4.65–126.3	4.50–53.5	3.72–51.3	5–125.278	10.39–132.0	4.12–53.6	4.47–51.5	4.28–51.19
Refl. collected	143006	13394	37445	30458	20533	52905	25374	73930
Independent refl.	33321 [R_{int} = 0.0706, R_σ = 0.0501]	5726 [R_{int} = 0.0325, R_σ = 0.0326]	27013 [R_{int} = 0.0526, R_σ = 0.0956]	16123 [R_{int} = 0.0400, R_σ = 0.0371]	11271 [R_{int} = 0.0792, R_σ = 0.0582]	14278 [R_{int} = 0.0888, R_σ = 0.0572]	11692 [R_{int} = 0.0729, R_σ = 0.0735]	11170 [R_{int} = 0.0801, R_σ = 0.0334]
Ind. refl. $I \geq 2\sigma(I)$	22111	4984	19530	14990	9333	10474	8350	9721
Data/rest./param.	33321/1/2058	5726/0/347	27013/13/2228	16123/2/1575	11271/0/852	14278/0/769	11692/100/838	11170/4/839
Gof	1.021	1.168	0.899	1.030	1.034	1.028	1.025	1.289
R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0571 wR_2 = 0.1531	R_1 = 0.0556 wR_2 = 0.1192	R_1 = 0.0462 wR_2 = 0.0781	R_1 = 0.0483 wR_2 = 0.1220	R_1 = 0.0905 wR_2 = 0.2356	R_1 = 0.0769 wR_2 = 0.2066	R_1 = 0.0909 wR_2 = 0.2343	R_1 = 0.0932 wR_2 = 0.2659
R indexes [all data]	R_1 = 0.0840 wR_2 = 0.1668	R_1 = 0.0656 wR_2 = 0.1225	R_1 = 0.0764 wR_2 = 0.0865	R_1 = 0.0533 wR_2 = 0.1273	R_1 = 0.1030 wR_2 = 0.2469	R_1 = 0.0955 wR_2 = 0.2275	R_1 = 0.1229 wR_2 = 0.2672	R_1 = 0.0995 wR_2 = 0.2817
Diff. peak/hole /$eÅ^{-3}$	0.69/–0.47	0.91/–0.79	0.64/–0.46	0.73/–0.91	5.62/–2.27	3.22/–3.98	2.07/–2.91	3.37/–3.20
Flack parameter	–	–	0.011(16)	–0.005(7)	–	–	–	–
CCDC no.	1847920	1847921	1847922	1847923	1847924	1847925	1847926	1847927

Table S1 (continued)

Comp.	**11a**	**11**·DCM (**11b**)	**12**·0.92cyhex ·¼DCM **(12a)**	**12**·½DCM (**12b**)	**12**·1½DCM (**12c**)	**13**·2acetone (**13a**)	**13**·3DCM (**13b**)
Emp. formula	$C_{68}H_{50}N_2O_4P_4Pd$	$C_{69}H_{52}Cl_2N_2O_4P_4Pd$	$C_{39.75}H_{36.5}Cl_{2.5}NO_2P_2Pd$	$C_{34.5}H_{26}Cl_3NO_2P_2Pd$	$C_{35.5}H_{28}Cl_5NO_2P_2Pd$	$C_{80}H_{74}F_{12}N_2O_8P_6Pd$	$C_{71}H_{56}Cl_6F_{12}N_2O_4P_6Pd$
Molar mass	1189.38	1274.30	817.16	761.25	846.18	1711.63	1734.09
Temperature/K	180.15	180.15	133.15	133.15	133.15	180.15	180.15
Crystal system	monoclinic	monoclinic	trigonal	monoclinic	triclinic	monoclinic	triclinic
Space group	C2/c	*Cc*	*R*3	$P2_1/c$	$P\bar{1}$	C2/c	$P\bar{1}$
a/Å	15.9829(7)	23.3882(11)	37.7119(13)	27.3505(14)	11.3516(8)	22.0681(10)	12.4072(5)
b/Å	15.0730(8)	11.1956(3)	37.7119(13)	17.7863(13)	15.8507(15)	17.9381(5)	12.7420(5)
c/Å	23.6619(13)	21.9982(9)	13.4414(4)	27.8832(14)	21.6322(19)	20.6378(8)	13.3068(6)
α/°	90	90	90	90	77.447(7)	90	73.232(3)
β/°	106.616(4)	97.454(4)	90	111.516(4)	76.796(6)	107.358(3)	85.908(3)
γ/°	90	90	120	90	71.073(7)	90	62.212(3)
Volume/Å^3	5462.4(5)	5711.4(4)	16555.1(12)	12619.0(13)	3540.9(6)	7797.6(5)	1777.01(14)
Z	4	4	18	16	4	4	1
ρ_{calc}g/cm^3	1.446	1.482	1.475	1.603	1.587	1.458	1.620
μ/mm^{-1}	0.511	0.585	0.809	0.978	1.026	0.446	0.705
F(000)	2440.0	2608.0	7497.0	6128.0	1700.0	3504.0	874.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range /°	4.51–53.5	4.35–52.0	3.74–52.2	2.90–52	2.75–52.0	4.54–53.5	4.48–53.5
Refl. collected	13297	25025	21904	88531	17569	17674	15533
Independent refl.	5731 [R_{int} = 0.0275, R_σ = 0.0314]	10274 [R_{int} = 0.0582, R_σ = 0.0612]	13281 [R_{int} = 0.0615, R_σ = 0.0660]	24787 [R_{int} = 0.0263, R_σ = 0.0227]	12139 [R_{int} = 0.0938, R_σ = 0.1672]	8147 [R_{int} = 0.0303, R_σ = 0.0369]	7429 [R_{int} = 0.0264, R_σ = 0.0246]
Ind. refl. I ≥ 2σ(I)	4579	8476	11200	19811	6584	6456	6622
Data/rest./param.	5731/0/337	10274/5/729	13281/34/850	24787/0/1567	12139/6/826	8147/108/492	7429/0/453
Gof	1.037	1.060	1.005	1.029	0.910	1.037	1.048
R indexes [I≥ 2σ(I)]	R_1 = 0.0365 wR_2 = 0.0909	R_1 = 0.0486 wR_2 = 0.1141	R_1 = 0.0628, wR_2 = 0.1518	R_1 = 0.0292 wR_2 = 0.0710	R_1 = 0.0722 wR_2 = 0.1617	R_1 = 0.0471 wR_2 = 0.1284	R_1 = 0.0418 wR_2 = 0.1061
R indexes [all data]	R_1 = 0.0500 wR_2 = 0.0954	R_1 = 0.0652 wR_2 = 0.1211	R_1 = 0.0746, wR_2 = 0.1584	R_1 = 0.0429 wR_2 = 0.0756	R_1 = 0.1428 wR_2 = 0.1834	R_1 = 0.0625 wR_2 = 0.1362	R_1 = 0.0469 wR_2 = 0.1093
Diff. peak/hole /eÅ^{-3}	0.96/–0.44	1.28/–0.97	1.65/–0.74	0.63/–0.56	1.29/–1.47	1.31/–0.97	1.40/–1.38
Flack parameter	–	–0.04(2)	0.45(4)	–	–	–	–
CCDC no.	1847928	1847929	1847930	1847931	1847932	1847933	1847934

Magnetic Measurements

Zero-Field-Cooled temperature dependent susceptibilities were recorded for **1** and **11** in dc mode using a MPMS-III (Quantum Design) SQUID magnetometer over a temperature range from 2 to 300 K in a homogeneous 0.1 T external magnetic field. The magnetization curves of **1** and **11** were measured on the same instrument up to a dc field of 7 T. Zero-Field-Cooled (ZFC) temperature dependent magnetic susceptibilities were recorded for **7** in RSO mode using a MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range from 2 to 150 K in a homogeneous external magnetic field of 0.5 T

The samples were contained in gelatine capsules filled in a glove box under argon atmosphere owing to the high degree of moisture and oxygen sensitivity of the compounds. The samples were transferred in sealed Schlenk tubes from the glove box to the magnetometer and then rapidly transferred to the helium-purged sample space of the magnetometer. The data were corrected for the sample holder including the gelatine capsule and for diamagnetism using Pascal's constants. [4,5,6]

The χT *vs T* and *M* versus *H* curves at different temperatures were simultaneously fitted using the PHI program [7] by means of an isotropic spin Hamiltonian (SH):

$$H = g\mu_B \vec{S}\vec{B} \qquad \text{eqn. S1}$$

S: spin operator; *B* magnetic induction; *g*: Landé factor; μ_B: Bohr magneton

Effects of intramolecular interaction (Θ_w) and temperature independent paramagnetism (TIP) are included by:

$$\chi = \frac{\chi_{calc} + TIP}{1 - \left(\frac{\Theta_W}{N_A \mu_B}\right)(\chi_{calc} + TIP)} \qquad \text{eqn. S2}$$

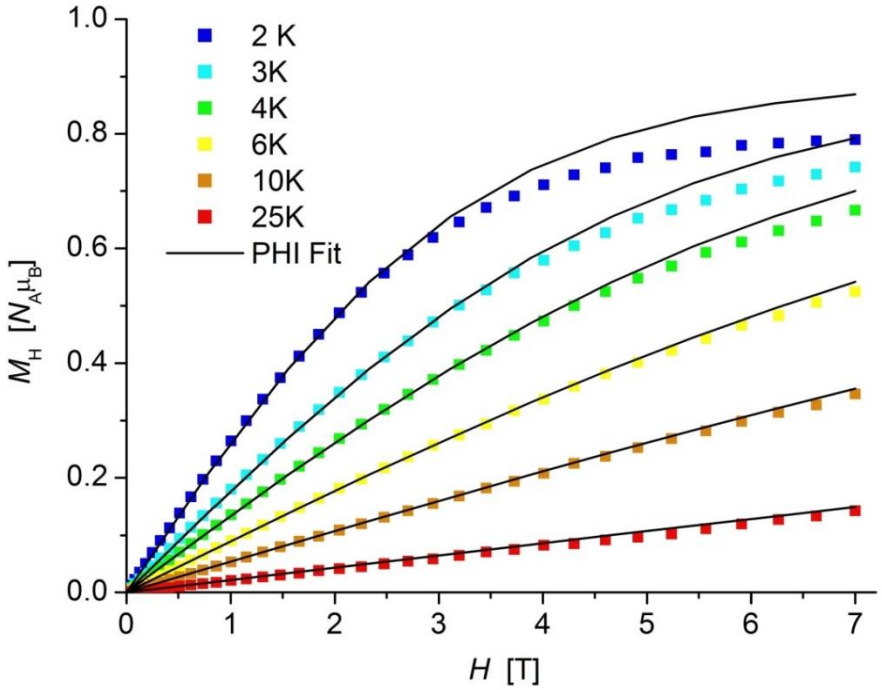

Figure S14 Plots of the magnetization *M* versus *H* for [Cu(**L1L1'**)] (**1**) at different temperatures. The solid lines represent the results of the simultaneous fits (eqn (S1)) with the PHI program.

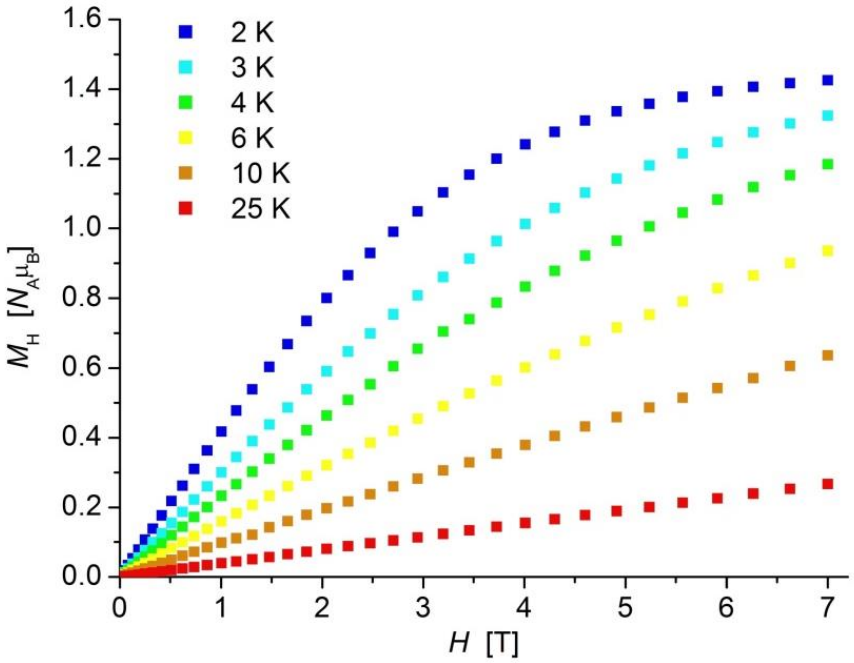

Figure S15 Plots of the magnetization *M* versus *H* for [Pd(**L1'**)$_2$] (**11**) at different temperatures.

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