Electronic Supporting information

The Coordination- and Photochemistry of Copper(I) Complexes: Variation of N^N Ligands from Imidazole to Tetrazole

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Content

1. Structural studies

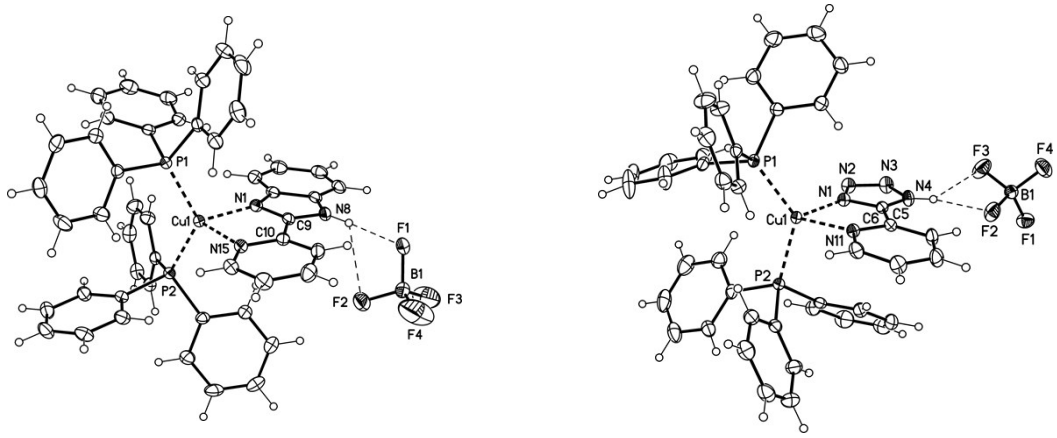


Figure S1. Molecular structures of $[(PyrBimH)Cu(PPh_3)_2]BF_4$ (**1**), and $[(PyrTetH)Cu(PPh_3)_2]BF_4$ (**3**), reproduced from Ref. 1[1] with permission from the Royal Society of Chemistry (displacement parameters are drawn at 50% probability level).

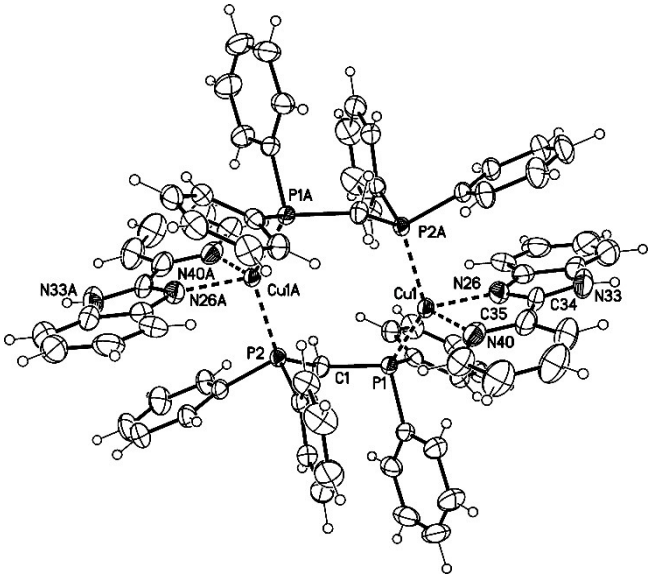


Figure S2. Molecular structure of $[(PyrBimH)_2Cu_2(dppm)_2](PF_6)_2$ (**4PF$_6$**) (displacement parameters are drawn at 50% probability level, solvent and anion omitted for clarity).

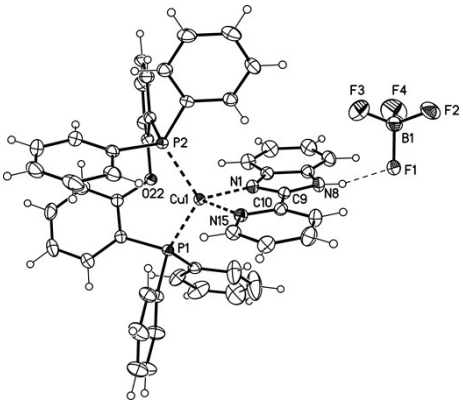


Figure S3. Molecular structures of [(PyrBimH)Cu(DPEPhos)]BF_4 (**5**) (displacement parameters are drawn at 50% probability level, solvent molecules omitted for clarity).

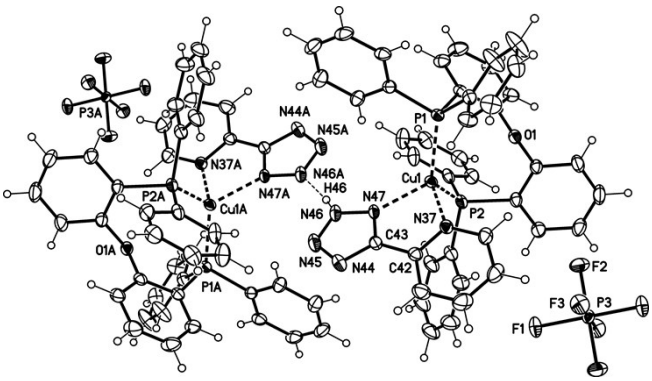


Figure S4. a) Molecular structure of [(PyrTetH)Cu(DPEPhos)][(PyrTet)Cu(DPEPhos)]PF_6 (**7PF$_6$**), reproduced from Ref. 1[1] with permission from the Royal Society of Chemistry (displacement parameters are drawn at 50% probability level).

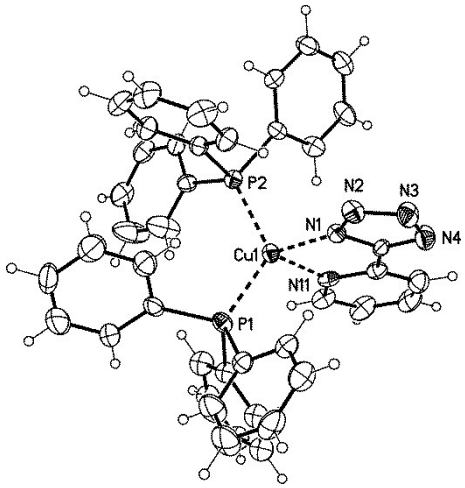
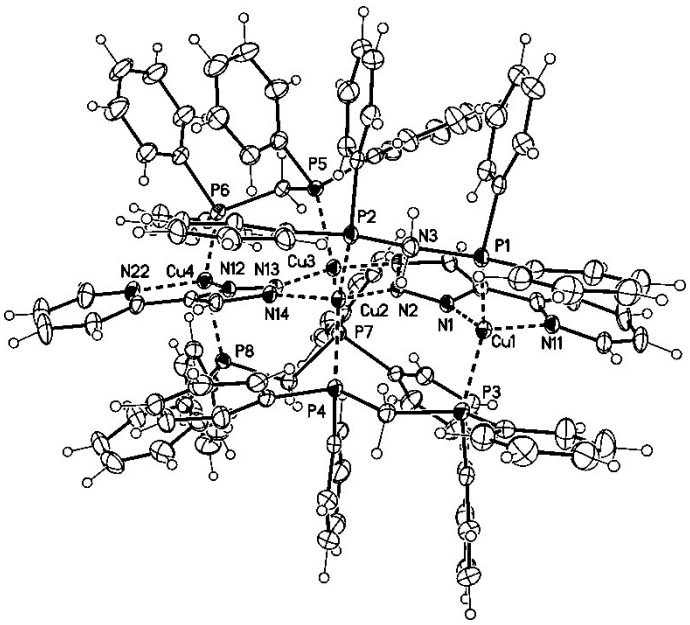


Figure S5. a) Molecular structure of [(5-(Pyridin-2-yl)tetrazolate)Cu(PPh_3)$_2$]BF_4 (**8**), reproduced from Ref. 1[1] with permission from the Royal Society of Chemistry (displacement parameters are drawn at 50% probability level).

a)



b)

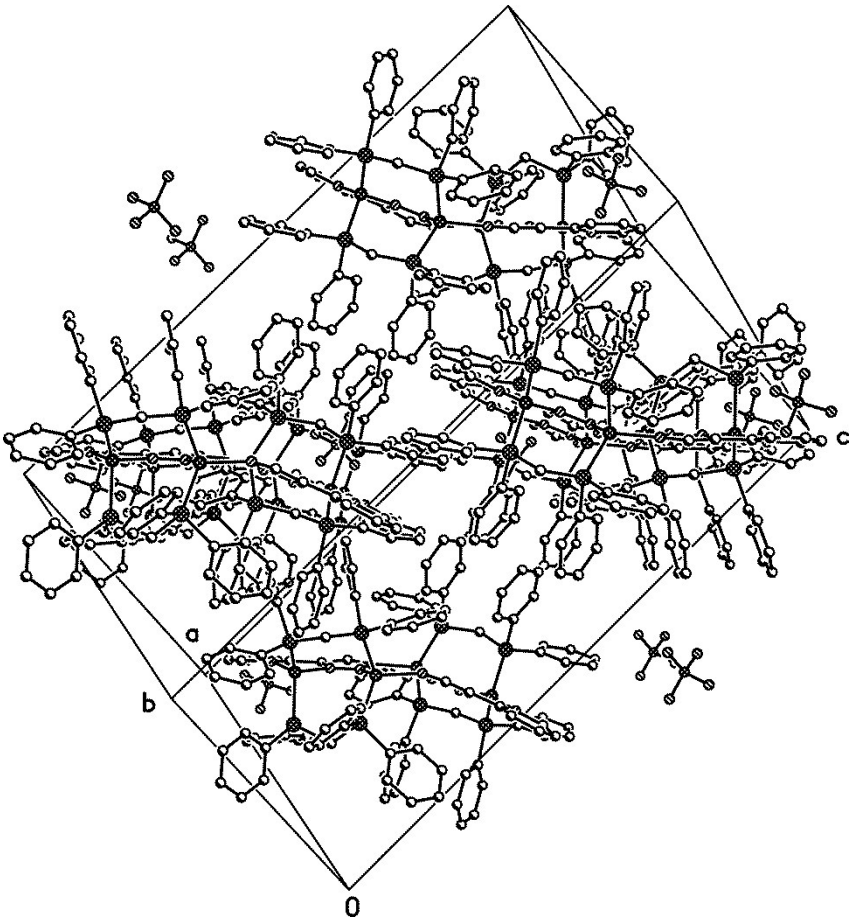
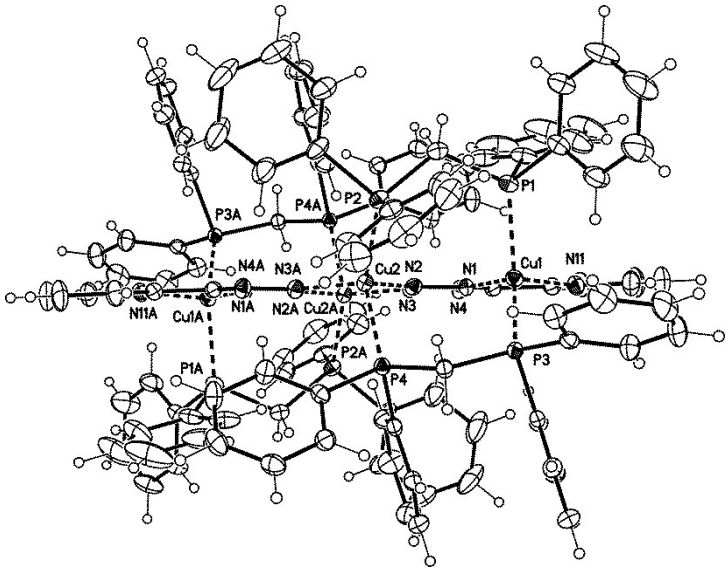


Figure S6. a) Molecular structure of **9** (displacement parameters are drawn at 50% probability level, anions omitted for clarity), b) crystal structure of $[(PyrTri)_2Cu_4(dppm)_4](BF_4)_2$ (**9**) (hydrogen atoms omitted for clarity).

a)



b)

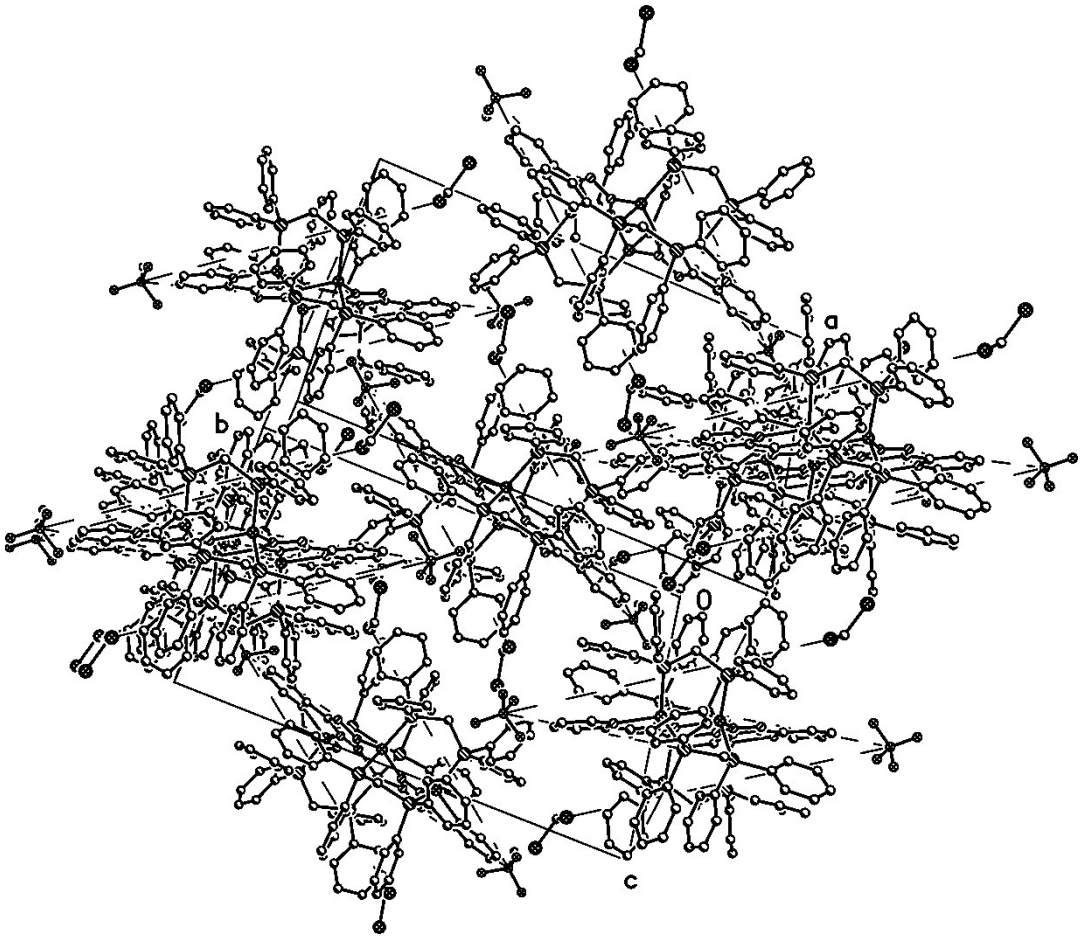


Figure S7. a) Molecular structure of **10** (displacement parameters are drawn at 50% probability level, anions and solvent omitted for clarity), b) crystal structure of $[(PyrTet)_2Cu_4(dppm)_4](BF_4)_2$ (**10**) (hydrogen atoms omitted for clarity).

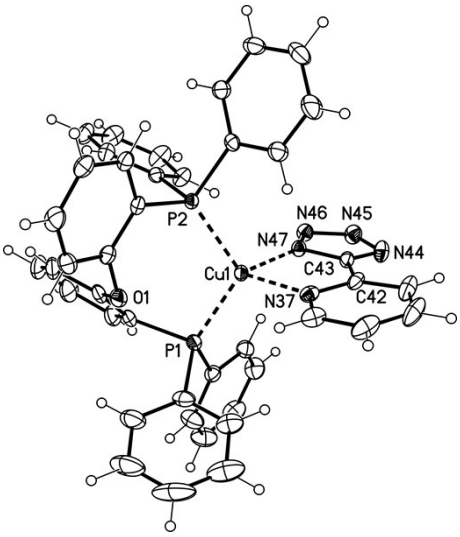


Figure S8. Molecular structures of the mononuclear complex [(PyrTet)Cu(DPEPhos)] (**13**) (displacement parameters are drawn at 50% probability level).

Table S1. Selected bond lengths (Å) and angles (°) of the structurally characterized dinuclear complex $[(PyrBimH)_2Cu_2(dppm)_2](PF_6)_2$ (**4PF$_6$**).

	bond lengths [Å]		**angles [°]**
Cu1-N26	2.083 (3)	N26-Cu1-N40	79.05 (11)
Cu1-N40	2.118 (3)	P1-Cu1-P2A	132.45 (3)
Cu1-P1	2.2087 (8)	φ_1[a]	89.21 (9)
Cu1-P2	2.2540 (8)	N26-C34-C35-N40	–3.3 (5)
P1-P2	3.121 (1)	P1-C1-P2	116.47 (15)
F1-H(N33)	2.24 (2)		
F3-H(N33)	2.46 (4)		
F6-H(N33)	2.35 (3)		
F3-H(C31)	2.47		
F6-H(C36)	2.40		

[a] Dihedral angle between N–Cu–N and P–Cu–P planes

Table S2. Selected bond lengths (Å) and angles (°) of the structurally characterized mononuclear complex $[(PyrTet)Cu(PPh_3)_2]$ (**8**).

	bond lengths [Å]		**angles [°]**
Cu1-N1	2.043 (4)	N1-Cu1-N11	79.82 (16)
Cu1-N11	2.118 (4)	P1-Cu1-P2	121.21 (6)
Cu1-P1	2.2397 (16)	φ_1[a]	83.4 (1)
Cu1-P2	2.2508 (15)	N1-C5-C6-N11	5.6 (7)
P1-P2	3.912 (2)		
N4-H(C15A)	2.50		

[a] Angle between N–Cu–N and P–Cu–P planes

Table S3. Selected bond lengths (Å) and angles (°) of the structurally characterized tetranuclear complexes $[(N^{\wedge}N)_2Cu_4(dppm)_4](BF_4)_2$ **9** and **10**.

	9	**10**
Cu1-N1	2.012 (2)	2.007 (2)
Cu1-N11	2.139 (2)	2.169 (2)
Cu1-P1	2.2528 (8)	2.2354 (8)
Cu1-P3	2.2223 (8)	2.1946 (8)
Cu2-N2	2.079 (2)	2.204 (2)
Cu2-N3A	2.065 (2)[a]	2.058 (2)
Cu2-P2	2.2722 (8)	2.2940 (8)
Cu2-P4	2.2810 (8)	2.3037 (8)
P1-P2	3.108 (1)	3.154 (1)
P3-P4	3.106 (1)	3.096 (1)
Cu1-Cu2	3.5974 (5)	3.5232 (6)
Cu2-Cu2A	3.9456 (6)[b]	4.4065 (9)
N1-Cu1-N11	78.66 (9)	78.69 (9)
P1-Cu1-P3	109.28 (3)	132.43 (3)
N2-Cu2-N3A	99.46 (9)[c]	87.38 (8)
P2-Cu2-P4	110.20 (3)	114.12 (3)
φ[q]	86.59 (5)/82.97 (5)	87.96 (6)/89.76 (6)
N1-C5-C6-N11	–9.5 (4)	1.9 (4)
P1-C24-P2	114.74 (15)[d]	117.20 (14)[e]

[a] Cu2-N14; [b] Cu2-Cu3; [c] N2-Cu2-N14; [d] P1-C35-P2; [e] P1-C12-P2.

2. **Photophysical Data**

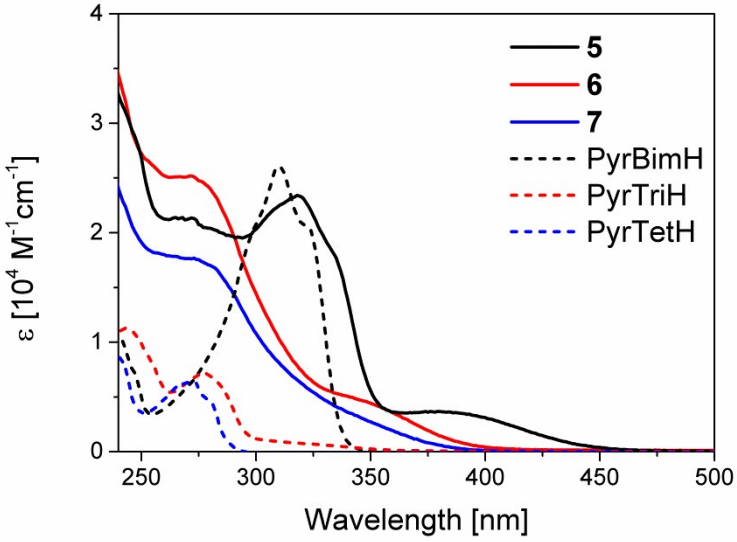


Figure S9. UV-Vis absorption spectra of complexes [(N^N)Cu(DPEPhos)]BF_4 **5–7** and free pyridine-amine ligands. The complexes **5–7** and PyrBimH are measured in CH_2Cl_2, PyrTriH and PyrTetH in EtOH at a concentration of 10^{-5} mol/l.

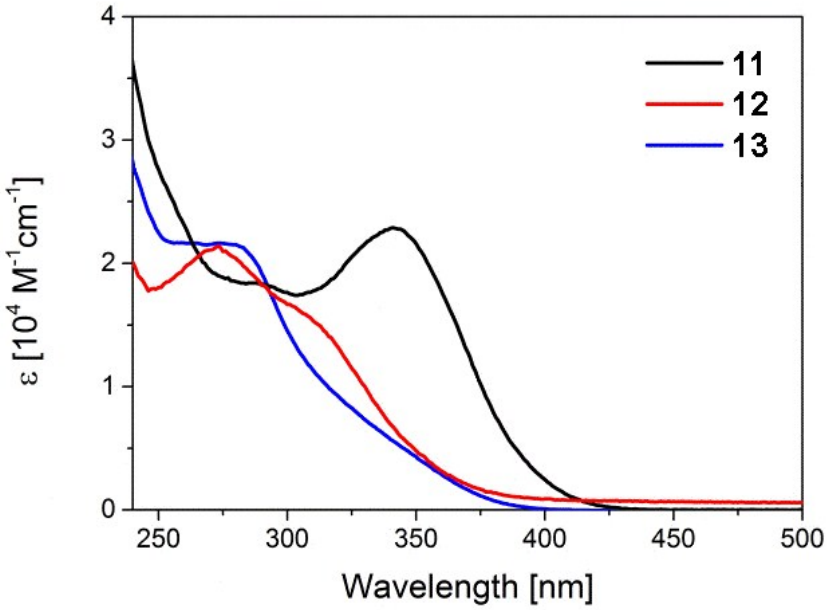


Figure S10. UV-Vis absorption spectra of complexes [(N^N)Cu(DPEPhos)] **11–13** in CH_2Cl_2 at a concentration of 10^{-5} mol/l.

Table S5. Excited state lifetimes of the complexes [(N^N)Cu(DPEPhos)]BF_4 **5–7** and [(N^N)Cu(DPEPhos)] **11–13** in the solid state.

Compound	τ_{ave}[a] [μs]	Compound	τ_{ave}[a] [μs]
5	5.1	**11**	18.4
6	26.8	**12**	9.6
7[b]	15.3	**13**[b]	19.9

[a] PL lifetime is composed of two components. For simplicity, a weighted-average lifetime was used (τ_{ave}) and calculated by the equation $\tau_{ave} = \Sigma A_i\tau_i/\Sigma A_i$ with A_i as the pre-exponential factor for the lifetime. [b] Reference [1].

3. Theoretical calculations

Table S6. Calculated HOMO and LUMO energies, as well as excitation energies as given by DFT. Geometries are optimized using the BP86 functional.[2, 3] Energies of the frontier orbitals are obtained by DFT calculations using the B3LYP functional[4-7] with def2-SV(P) basis set,[8, 9] and the excitation energies are calculated by TD-B3LYP.

complex	HOMO [eV]	LUMO [eV]	$\Delta E_{HOMO-LUMO}$ [eV]	Excitation energy [eV]
5	–7.74 eV	–4.63 eV	3.11 eV	2.53
6	–7.85 eV	–4.33 eV	3.52 eV	2.91
7	–8.18 eV	–4.71 eV	3.47 eV	2.87
11	–4.75 eV	–1.14 eV	3.61 eV	3.06
12	–5.23 eV	–1.19 eV	4.04 eV	3.23
13	–5.41 eV	–1.37 eV	4.04 eV	3.28

4. Crystallographic Data

The single-crystal X-ray diffraction studies of were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation (λ = 0.71073 Å) (**1**, **4PF$_6$**, **5**, **10, 11**)

on a Bruker-Nonius APEXII at 123(2) K using MoKα radiation (λ = 0.71073 Å) (**2PF$_6$**) and on a Bruker D8 Venture Diffractometer with Photon100 detector at 123(2) K using CuKα radiation (λ = 1.54178 Å) (**6, 9**).

Patterson Methods (**1**, **2PF$_6$**, **10**) or Direct Methods (**4PF$_6$**, **5**, **6**, **9**, **11**) (SHELXS-97[10]) were used for structure solution and refinement was carried out using SHELXL-97/2013/2014[11] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free. Semi-absorption corrections were applied for all structures.

In **2PF$_6$** one phenyl group and the anion PF_6 are disordered, in **5** the solvent CH_2Cl_2 is disordered about a center of symmetry, in **6** the solvent Et_2O is disordered about a 2-fold axis, in **9** the BF_4 anions are disordered, and in **10** the solvent CH_2Cl_2 is disordered.

In **9** the refinement with the listed atoms shows residual electron density due to heavily disordered solvent molecules in one void, which could not be refined with split atoms. The solvent molecules could be Et_2O or CH_2Cl_2 and some additional water. The number and kind of solvent molecules in the void could not be determined. Therefore the option "SQUEEZE"[12] of the program package PLATON[13] was used to create a hkl file taking into account the residual electron density in the void areas. Due to the unknown amount and kind of solvent, the solvent was not included in the unit card.

11 is a weak scattering crystal of bad quality (only 56.6 % are observed at 2θ = 55°), therefore only the conformation and important structural parameters could be discussed reliably.

1: yellow crystals, $C_{48}H_{39}CuN_3P_2 \cdot BF_4$, M = 870.11, crystal size 0.50 x 0.45 x 0.40 mm, T = 123(2) K, triclinic, space group P-1 (No. 2), a = 11.278(1) Å, b = 12.684(1) Å, c = 16.171(1) Å, α = 83.52(1)°, β = 76.41(1)°, γ = 66.60(1)°, V = 2063.1(3) Å^3, Z = 2, ρ(calc) = 1.401 Mg m^{-3}, F(000) = 896, μ = 0.664 mm^{-1}, 26082 reflections ($2\theta_{max}$ = 55°), 9426 unique [R_{int} = 0.021], 535 parameters, 1 restraint, $R1$ (for 7867 $I > 2\sigma(I)$) = 0.033, *wR2 (all data)* = 0.084, S = 1.02, largest diff. peak and hole 0.828 and -0.551 e Å^{-3}.

2PF$_6$:colourless crystals, $C_{43}H_{36}CuN_4P_2 \cdot PF_6$, M = 879.21, crystal size 0.50 x 0.30 x 0.25 mm, T = 123(2) K, triclinic, space group P-1 (No. 2), a = 12.0277(5) Å, b = 12.9010(5) Å, c = 14.6324(5) Å, α = 100.140(2)°, β = 113.803(2)°, γ = 94.065(2)°, V = 2019.36(14) Å^3, Z = 2, ρ(calc) = 1.446 Mg m^{-3}, F(000) = 900, μ = 0.724 mm^{-1}, 22436 reflections ($2\theta_{max}$ = 55°), 9143 unique [R_{int} = 0.031], 503 parameters, 681 restraints, $R1$ (for 8193 $I > 2\sigma(I)$) = 0.064, *wR2 (all data)* = 0.173, S = 1.06, largest diff. peak and hole 1.279 and -1.485 e Å^{-3} (in disordered PF_6 anion).

4PF$_6$:pale yellow crystals, $C_{74}H_{62}Cu_2N_6P_4 \cdot 2\ PF_6 \cdot 2\ C_4H_{10}O$, M = 1724.44, crystal size 0.35 x 0.15 x 0.10 mm, T = 123(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 15.024(1) Å, b = 14.129(2) Å, c = 19.206(2) Å, β = 108.60(1)°, V = 3864.0(7) Å^3, Z = 2, ρ(calc) = 1.482 Mg m^{-3}, F(000) = 1776, μ = 0.756 mm^{-1}, 53397 reflections ($2\theta_{max}$ = 55°), 8841 unique [R_{int} = 0.041], 499 parameters, 100 restraints, $R1$ (for 7092 $I > 2\sigma(I)$) = 0.052, *wR2 (all data)* = 0.145, S = 1.03, largest diff. peak and hole 1.239 and -1.686 e Å^{-3}.

5:yellow crystals, $C_{48}H_{37}CuN_3OP_2 \cdot 2\ BF_4 \cdot 0.5\ CH_2Cl_2$, M = 926.56, crystal size 0.60 x 0.40 x 0.35 mm, T = 123(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 11.423(1) Å, b = 14.922(2) Å, c = 25.552(3) Å, β = 95.86(1)°, V = 4332.7(9) Å^3, Z = 4, ρ(calc) = 1.420 Mg m^{-3}, F(000) = 1900, μ = 0.698 mm^{-1}, 62632 reflections ($2\theta_{max}$ = 55°), 9942 unique [R_{int} = 0.020], 566 parameters, 22 restraints, $R1$ (for 8922 $I > 2\sigma(I)$) = 0.037, *wR2 (all data)* = 0.089, S = 1.06, largest diff. peak and hole 0.836 and -0.730 e Å^{-3}.

6:yellow crystals, $C_{43}H_{34}CuN_4OP_2 \cdot BF_4 \cdot 0.5\ C_4H_{10}O$, M = 872.09, crystal size 0.16 x 0.10 x 0.06 mm, T = 123(2) K, monoclinic, space group C2/c (No. 15), a = 23.3084(8) Å, b = 15.1103(8) Å, c = 23.8529(10) Å, β = 98.530(2)°, V = 8308.0(6) Å^3, Z = 8, ρ(calc) = 1.394 Mg m^{-3}, F(000) = 3592, μ = 1.972 mm^{-1}, 56053 reflections ($2\theta_{max}$ = 144.2°), 8177 unique [R_{int} = 0.037], 553 parameters, 62 restraints, $R1$ (for 7290 $I > 2\sigma(I)$) = 0.031, *wR2 (all data)* = 0.084, S = 1.03, largest diff. peak and hole 0.664 and -0.338 e Å^{-3}.

9: colourless crystals, $C_{114}H_{98}Cu_4N_8P_8 \cdot 2\ BF_4$, M = 2255.54, crystal size 0.28 x 0.20 x 0.08 mm, T = 123(2) K, triclinic, space group P-1 (No. 2), a = 12.7716(6) Å, b = 15.7488(7) Å, c = 28.7966(13) Å, α = 87.544(2)°, β = 80.793(2)°, γ = 71.984(2)°, V = 5437.0(4) Å^3, Z = 2, ρ(calc) = 1.378 Mg m^{-3}, F(000) = 2312, μ = 2.527 mm^{-1}, 68531 reflections ($2\theta_{max}$ = 136.6°), 19857 unique [R_{int} = 0.036], 1287 parameters, 396 restraints, $R1$ (for 17026 $I > 2\sigma(I)$) = 0.045, *wR2 (all data)* = 0.116, S = 1.02, largest diff. peak and hole 1.402 and -1.037 e Å^{-3} (in disordered BF_4 anion).

10: pale green crystals, $C_{112}H_{96}Cu_4N_{10}P_8 \cdot 2\ BF_4 \cdot 2\ CH_2Cl_2$, M = 2427.37, crystal size 0.32 x 0.16 x 0.08 mm, T = 123(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 15.264(2) Å, b = 22.970(3) Å, c = 17.299(3) Å, β = 113.43(1)°, V = 5565.2(15) Å^3, Z = 2, ρ(calc) = 1.449 Mg m^{-3}, F(000) = 2480, μ = 1.032 mm^{-1}, 56450 reflections ($2\theta_{max}$ = 55°), 12758 unique [R_{int} = 0.038], 693 parameters, 49 restraints, $R1$ (for 10071 $I > 2\sigma(I)$) = 0.045, *wR2 (all data)* = 0.112, S = 1.03, largest diff. peak and hole 1.236 and -0.950 e Å^{-3} (in disordered solvent CH_2Cl_2).

11:yellow crystals, $C_{48}H_{36}CuN_3OP_2$, M = 796.28, crystal size 0.30 x 0.08 x 0.04 mm, T = 123(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 9.144(1) Å, b = 18.331(2) Å, c = 23.049(2) Å, β = 95.93(1)°, V = 3842.8(7) Å^3, Z = 4, ρ(calc) = 1.376 Mg m^{-3}, F(000) = 1648, μ = 0.694 mm^{-1}, 32257 reflections ($2\theta_{max}$ = 55°), 8809 unique [R_{int} = 0.116], 496 parameters, 777 restraints (general ISOR and rigid group restraints), $R1$ (for 4986 $I > 2\sigma(I)$) = 0.110, *wR2 (all data)* = 0.309, S = 1.05, largest diff. peak and hole 2.971 and -1.689 e Å^{-3} (near Cu).

This material is available free of charge via the Internet. Detailed crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1047149 (**1**), CCDC 1047150 (**2PF6**), CCDC-922231 (**3**) was already published,[1] CCDC 1047151 (**4PF6**), CCDC 1047152 (**5**), CCDC 1047153 (**6**), CCDC-922233 (**7PF6**) was already published,[1] CCDC CCDC-922230 (**8**) was already published,[1] CCDC 1047156 (**9**), CCDC 1047158 (**10**), CCDC and CCDC 1047160 (**11**), CCDC-922232 (**13**) was already published.[1] Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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