Supporting Information

A Copper(I) Complex with Two Unpaired Electrons, Synthesised by Oxidation of a Copper(II) Complex with Two Redox-Active Ligands

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Supporting Information

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1. General Experimental Details

If not otherwise stated all synthetic work was carried out under dry argon atmosphere using the Schlenk technique. The applied solvents were dried with an MBraun Solvent Purification System, degassed by three freeze-pump-thaw cycles and stored over molecular sieves prior to their use. The used chemicals were obtained from common companies (Sigma-Aldrich, Acros Organics, Alfa Aesar, abcr GmbH and TCI). Elemental analysis was performed at the Microanalytical Laboratory of the University of Heidelberg using the vario EL and vario MICRO cube devices from Elementar Analysensysteme GmbH. NMR spectra were recorded on a Bruker DPX 200, Bruker Avance II 400 spectrometer or Bruker Avance III 600 spectrometer. Solvent resonances were taken as references for all $^1$H NMR or $^{13}$C NMR spectra. HR-ESI spectra were recorded with a Bruker ApexQe hybrid 9.4 T FT-ICR spectrometer. HR-El spectra were recorded with a JEOL AccuTOF GCx instrument. UV-Vis-NIR measurements relied on a VARIN Cary 5000 spectrophotometer. CV measurements were carried out at a Metrohm Autolab PGSTAT 204 potentiostate/galvanostate with an Ag/AgCl reference electrode. The curves were recorded at room temperature. CH$_2$Cl$_2$ was used as solvent for the individual compounds (c = 10$^{-3}$ M), whereas nBu$_4$N(PF$_6$) (electrochemical grade (≥99.0%)) was employed as supporting electrolyte (c = 0.1 M), a Pt rod counter electrode and glassy carbon working electrode were used. Spectra were referenced externally by the Fc$^+$/Fc redox couple. X-band EPR spectra were measured with a Bruker Elexsys E500 EPR with an ER 4116DM CW dual mode resonator. As temperature system an ER 4112HV-CF58nc In-Cavaty Cryogen Free VT is used. The dc-SQUID measurements were taken with a MPMS-XL apparatus from LOT Quantum Design. The single oxidised Cu complexes have been characterized by X-ray photoelectron spectroscopy. The measurements were performed with a laboratory spectrometer equipped with a non-monochromatized Mg Kα X-ray source (200 W) and a EA 15 hemispherical analyser (Prevac, Poland). The samples were prepared by drop-casting of the Cu complexes dissolved in dichloromethane onto Au substrates. The amount of the deposited material varied to some extent from sample to sample. The exposure of the deposited material to ambient during their loading into the spectrometer was kept as short as possible. The binding energy scale of the XP spectra was referenced to the Au 4f7/2 emission at 84.0 eV.$^{[S1]}$ The spectra were processed with the xpspeak41 program (public domain). The processing included a background correction and decomposition of the spectra and individual features by suitable combinations of Voigt peaks. GC/MS measurements were carried out using helium as carrier gas on an Agilent 6890 Series gas chromatograph with an HP-5MS column (5 % diphenylpolysiloxane and 95 % dimethylpolysiloxane; dimensions 30 m x 0.25 mm x 0.25 μm) and an Agilent 5973 Mass Selective detector.

DFT calculations

DFT calculations were carried out with the TURBOMOLE program package.$^{[S2]}$ The B3LYP functional$^{[S3]}$ in combination with the def2-TZVP basis set$^{[S4]}$ was used in all calculations. Structural optimizations were performed at the RI-DFT$^{[S5]}$ level of theory. Dispersion is included by the DFT-D3 $^{[S6]}$ approach developed by Grimme and co-workers. For all structures calculated a vibrational analysis was carried out to confirm that the optimized structures are energy minima on the potential energy hypersurface. Time-dependent density functional theory (TD-DFT) computations$^{[S7,S8,S9]}$ for the radicals L1$^-$ and L2$^-$ (S = 1/2) were performed to obtain the vertical

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[S1] J. F. Moulder, W. E. Stickle, P. E. Sobol, K. D. Bomben Handbook of X-ray Photoelectron Spectroscopy, J. Chastian (Ed.); Perkin-Elmer Corp.: Eden Prairie, MN, 1992.
[S2] TURBOMOLE, vers. 7.4.1 2019, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[S3] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. 1988, 37, 785.
[S4] A. Schäfer, H. Horn, R. Ahrlichs, J. Chem. Phys. 1992, 97, 2571.
[S5] O. Treutler, R. Ahrlichs, J. Chem. Phys. 1995, 102, 346.
[S6] S. Grimme, J. Comput. Chem. 2004, 25, 1463.
[S7] R. Bauernschmitt, M. Häser, O. Treutler, R. Ahrlichs, Chem. Phys. Lett. 1997, 264, 573.
[S8] E. Runge, E. K. U. Gross, Phys. Rev. Lett. 1984, 52, 997.
[S9] R. Bauernschmitt, R. Ahrlichs, Chem. Phys. Lett. 1996, 256, 454.
excitations energies and oscillator strength in order in interpret electronic excitation spectrum of the oxidised copper complexes. Within these computations, the excitation energies for the first 40 states were determined.
2. Experimental Details and some analytical data for all compounds (see also detailed analytical data in section 3)

Synthesis of HL1 in 2 Steps:

Step 1

The hydrazone was synthesised according to a literature procedure.[1] In a pyrex pressure vessel 2-chloro-1-methyl-1H-benzo[d]imidazole,[2] (1.85 g, 11.1 mmol) and hydrazinium hydroxide (~100%, 2.7 ml, 55.7 mmol) were suspend in ethanol (6 ml). The closed vessel was stirred at 110 °C for 12 h. The resulting solution was triturated with MTBE (20 ml), the precipitate was filtered and dried under vacuum affording the product as colourless plates (1.63 g, 10.1 mmol, 91%).

\[ \text{NMR} (200.18 \text{ MHz, DMSO-d6, 298 K}): \delta = 7.27-7.15 (\text{m}, 2 \text{ H, CH} \text{arom}), 6.98-6.93 (\text{m}, 2 \text{ H, CH} \text{arom}), 3.47 (\text{s}, 3 \text{ H, CH}_3) \text{ ppm.} \]

Step 2

1-Methyl-2,3-dihydro-1H-benzo[d]imidazole hydrazone (500 mg, 3.08 mmol, 1 eq.) and 2-chloro-1,3-dimethylimidazolinium chloride (521 mg, 3.08 mmol, 1 eq.) were suspended in CH\(_2\)Cl\(_2\) (12 ml) at 0 °C. Subsequently NEt\(_3\) (2.6 ml, 18.5 mmol, 6 eq.) was added and the reaction mixture was stirred at 0 °C for 10 min and afterwards allowed to warm to room temperature and stirred for 2.5 h. Aqueous NaOH (2 M, 1 g, 25 mmol, 8.1 eq) and water (20 ml) were added. The mixture was extracted with CH\(_2\)Cl\(_2\) (2 x 5 ml) and the organic layer was then transferred into a purged Schlenk flask and the solvent removed in vacuo. Blueish-white powder (563 mg, 2.18 mmol, 71%). Crystals suitable for XRD analysis can be derived by solving the crude in 1,2-difluorobenzene and layering with n-pentane.

\[ \text{NMR} (600.13 \text{ MHz, CD}_2\text{Cl}_2, 293 K): \delta = 8.64 (\text{bs}, 1 \text{ H, NH}), 6.90-6.88 (\text{m}, 1 \text{ H, CH} \text{arom}), 6.83-6.81 (\text{m}, 2 \text{ H, CH} \text{arom}), 6.76-6.75 (\text{m}, 1 \text{ H, CH} \text{arom}), 3.37 (\text{s}, 3 \text{ H, CH}_3), 3.27 (\text{s}, 3 \text{ H, CH}_3), 3.18-3.15 (\text{m}, 4 \text{ H, CH}_2), 2.75 (\text{s}, 3 \text{ H, CH}_3) \text{ ppm.} \]

\[ \text{NMR} (150.93 \text{ MHz, CD}_2\text{Cl}_2, 295 K): \delta = 157.4 (C_q, C_{\text{gua}}), 135.1 (C_q, C_{\text{arom}}/C_{\text{gua}}), 120.4 (C_H, C_{\text{arom}}), 120.3 (C_H, C_{\text{arom}}), 116.9 (C_H, C_{\text{arom}}), 107.8 (C_q, C_{\text{arom}}), 105.5 (C_H, C_{\text{arom}}), 51.4 (C_H), 49.5 (C_H), 38.5 (C_H), 35.4 (C_H), 27.8 (C_H) \text{ ppm.} \]

HR-MS (EI\(^+\)): m/z calcd. for C\(_{13}\)H\(_8\)N\(_6\) [M\(^+\)]\(^+\) 258.1587, found 258.1590.
Synthesis of HL2 in 2 Steps:

**Step 1**

The hydrazone was synthesised according to a literature procedure.[1] In a round bottom flask 2-aminobenzothiazole (2.55 g, 17 mmol, 1 eq.), hydrazinium hydroxide (~100%, 9.5 ml, 196 mmol) were suspended in ethylene glycol (15 ml) and conc. HCl\textsubscript{aq} (12 M, 1.25 ml, 15.0 mmol) was added. The mixture was stirred at 130 °C for 5 h. After cooling to room-temperature the product precipitates as colourless needles and was collected by filtration, washed with EtOH (7 ml) and dried under vacuum, yielding 927 mg (5.61 mmol, 32%).

**1H NMR** (600.18 MHz, DMSO-d\textsubscript{6}, 295 K): \(\delta = 9.01\) (s, 1 H, NH), \(7.68 - 7.66\) (m, 1 H, CH\textsubscript{arom}), \(7.32 - 7.30\) (m, 1 H, CH\textsubscript{arom}), \(7.21 - 7.18\) (m, 1 H, CH\textsubscript{arom}), \(6.99 - 6.96\) (m, 1 H, CH\textsubscript{arom}), \(5.02\) (s, 2 H, NH\textsubscript{2}) ppm.

**Step 2**

Benzo[d]thiazol(3H) hydrazone (500 mg, 3.03 mmol, 1 eq.) and 2-chloro-1,3-dimethylimidazolinium chloride (512 mg, 3.03 mmol, 1 eq.) were suspended in CH\textsubscript{2}Cl\textsubscript{2} (12 ml) at 0°C. Subsequently NEt\textsubscript{3} (3.4 ml, 24.21 mmol, 8eq.) was added and the reaction mixture was stirred at 0°C for 10 min and afterwards allowed to warm to room temperature and stirred for 5 h. Aqueous NaOH (2 M, 1.45 g, 36.32 mmol, 12 eq.) and water (20 ml) were added. The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (2x5 ml) and the organic layer was then transferred into a purged Schlenk flask and the solvent removed in vacuo. Greenish-white powder (590 mg, 2.26 mmol, 75%).

**1H NMR** (600.18 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 295 K): \(\delta = 9.69\) (bs, 1 H, NH), 7.49-7.48 (m, 1 H, CH\textsubscript{arom}), 7.32-7.30 (m, 1 H, CH\textsubscript{arom}), 7.21-7.18 (m, 1 H, CH\textsubscript{arom}), 6.99-6.96 (m, 1 H, CH\textsubscript{arom}), 5.02 (s, 2 H, NH\textsubscript{2}) ppm.

**13C\textsuperscript{[1]H] NMR** (150.93 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 295 K): \(\delta = 159.0\) (C\textsubscript{q}, C\textsubscript{gua}), 148.2 (C\textsubscript{q}, C\textsubscript{arom}/C\textsubscript{guaS}), 128.6 (C\textsubscript{q}, C\textsubscript{arom}/C\textsubscript{guaS}), 125.9 (CH, C\textsubscript{arom}), 121.7 (CH, C\textsubscript{arom}), 120.5 (CH, C\textsubscript{arom}), 114.8 (CH, C\textsubscript{arom}), 51.3 (CH\textsubscript{2}), 48.9 (CH\textsubscript{2}), 37.4 (CH\textsubscript{3}), 34.6 (CH\textsubscript{3}) ppm.

**HR-MS** (ESI\textsuperscript{+}, MeCN): \(m/z\) calcd for C\textsubscript{12}H\textsubscript{16}N\textsubscript{5}S\textsuperscript{+} [M+H]\textsuperscript{+} = 262.1121, found \(m/z = 262.1122\).
Synthesis of [Zn(L1)2]

\[
\text{HL1 (296 mg, 1.15 mmol, 2 eq.) was dissolved in o-difluorobenzene (5 ml) at 0°C, subsequently Zn(Et)₂ in n-hexane (1 M, 250 µl, 0.25 mmol, 1 eq.) was added dropwise and the solution was degassed three times. After 1 h the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. All volatiles were removed in vacuo and the residue was washed with Et₂O (3x3 ml). The residue was dried in vacuo, yielding the product as a colourless powder (241 mg, 0.42 mmol, 73 %). Crystals suitable for XRD analyses were obtained by layering a concentrated solution of [Zn(L1)2] with n-pentane.}
\]

\[\text{1H NMR (399.89 MHz, CD₂Cl₂, 295 K): } \delta = 6.74-6.66 (m, 8 H, CHₐrom), 3.42 (s, 6 H, CH₃), 3.33 (s, 6 H, CH₃), 3.31-3.20 (m, 8 H, CH₂), 2.61 (s, 6 H, CH₃) ppm.\]

\[\text{13C[¹H] NMR (100.56 MHz, CD₂Cl₂, 295 K): } \delta = 160.5 (Cₗq, Cₐrom), 160.2 (Cₗq, Cₐrom), 140.8 (Cₗq, Cₐrom), 137.7 (Cₗq, Cₐrom), 119.5 (CH, Cₐrom), 117.5 (CH, Cₐrom), 109.6 (CH, Cₐrom), 104.7 (CH, Cₐrom), 51.2 (CH₂), 50.5 (CH₂), 38.6 (CH₃), 36.3 (CH₃), 27.8 (CH₃) ppm.\]

\[\text{UV-vis (CH₂Cl₂): } \lambda_{\text{max}} (\varepsilon \text{ in L mol}^{-1} \text{ cm}^{-1}) = 235 (6.58\times 10^4), 284 (3.41\times 10^4), 337 (6.93\times 10^4) \text{ nm.}\]

Elemental analysis (C₂₆H₃₄ZnN₁₂, MW: 580.02 g mol⁻¹):

calcd. C 53.84, H 5.91, N 28.98; found C 53.79, H 6.00, N 28.68.

Neutral Cu(II)-Complexes

Synthesis of [Cu(L1)²]

\[
\text{The protonated ligand HL1 (150 mg, 0.58 mmol, 2 eq.), Cu(OAc)₂ (53 mg, 0.29 mmol, 1 eq.) and KO'Bu (65 mg, 0.29 mmol, 2 eq.) were mixed and tetrahydrofuran (4 ml) was added. The reaction}
\]
mixture was stirred for 18 h resulting in a green suspension. All volatiles were removed in vacuo and the residue was dissolved in CH$_2$Cl$_2$ (4 ml). The solution was filtered to remove the KOAc by-product. Then, the filtrate was concentrated, and the resulting green residue was washed with MeCN (2x3 ml) and Et$_2$O (2x3 ml). The residue was dried in vacuo, yielding the product as a green powder (111 mg, 0.168 mmol, 66%). Further purification and crystals suitable for XRD analyses were achieved by dissolving the crude in CH$_2$Cl$_2$ and layering with n-pentane (green to purple crystals).

**UV-vis** (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε in L mol$^{-1}$ cm$^{-1}$) = 243 (2.11x10$^4$), 338 (2.11x10$^4$), 450 (0.16x10$^4$), 650 (0.12x10$^4$), 1845 (0.04x10$^4$) nm.

**Elemental analysis** (C$_{26}$H$_{34}$CuN$_{12}^{*}0.15$ CH$_2$Cl$_2$):
calcd. C 53.15, H 5.85, N 28.44; found C 52.99, H 6.26, N 28.24.

**Synthesis of [Cu(L2)$_2$]**

The protonated ligand HL2 (150 mg, 0.57 mmol, 2 eq.), Cu(OAc)$_2$ (52 mg, 0.29 mmol, 1 eq.) and KO'Bu (64 mg, 0.57 mmol, 2 eq.) were mixed and tetrahydrofuran (4 ml) was added. The reaction mixture was stirred for 16 h resulting in a green suspension. All volatiles were removed in vacuo and the residue was dissolved in CH$_2$Cl$_2$ (4 ml). Then, the solution was filtered to remove the KOAc by-product. The filtrate was concentrated, and the resulting green residue washed with MeCN (1x3 ml) and Et$_2$O (2x3ml). The residue was dried in vacuo, yielding the product as a dark green powder (45 mg, 0.08 mmol, 27%). Further purification and crystals suitable for XRD analyses were achieved by dissolving the product in CH$_2$Cl$_2$ and layering the solution with Et$_2$O (green crystals).

**UV-vis** (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε in L mol$^{-1}$ cm$^{-1}$) = 229 (4.89x10$^4$), 324 (5.55x10$^4$), 450 (0.16x10$^4$), 559 (0.12x10$^4$), 609 (0.18x10$^4$), 1880 (0.05x10$^4$) nm.

**Elemental analysis** (C$_{24}$H$_{28}$CuN$_{10}$S$_2$, $MW$: 584.22 g mol$^{-1}$):
calcd. C 49.34, H 4.83, N 23.98; found C 49.63, H 5.01, N 23.86.
**Single-oxidised complexes**

[Cu(L1)2]SbF$_6$ [Cu(L1)2] (53.5 mg, 0.09 mmol, 1 eq.) and AgSbF$_6$ (32.5 mg, 0.1 mmol, 1.02 eq.) were treated with CH$_2$Cl$_2$ (3 ml). The deep purple reaction mixture was stirred for 23 h and filtered under argon. The solvent was removed *in vacuo* and the residue was washed with Et$_2$O (2*3 ml). The crude product was obtained as a dark powder. Crystals suitable for XRD analysis were obtained by dissolving the product in 1,2-difluorobenzene and layering the solution with *n*-pentane.

[Cu(L1)2]PF$_6$ [Cu(L1)2] (55 mg, 0.09 mmol, 1 eq.) was dissolved in CH$_2$Cl$_2$ (3 ml). FcPF$_6$ (31.5 mg, 0.095 mmol, 1 eq.) was added, resulting in a deep purple reaction mixture which was stirred for 3 h. The solvent was removed *in vacuo* and the residue was washed with Et$_2$O (4x3 ml) and *n*-hexane (3 ml). The product was obtained as a dark powder (57 mg, 0.079 mmol, 83 %).

**Paramagnetic $^1$H NMR** (399.89 MHz, CD$_2$Cl$_2$, 298.2 K): $\delta = 109.0$ (bs, 8 H, CH$_2$), 67.8 (s, 12 H, NCH$_3$), 66.2 (s, 6 H, NCH$_3$), 10.5 (s, 2 H, CH$_{arom.}$), $-11.8$ (s, 2 H, CH$_{arom.}$), $-45.7$ (s, 2 H, CH$_{arom.}$), $-75.6$ (s, 2 H, CH$_{arom.}$) ppm.

**UV-vis** (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε in L mol$^{-1}$ cm$^{-1}$) = 230 (2.82x10$^4$), 295 (1.30x10$^4$), 365 (2.77x10$^4$), 505 (1.04x10$^4$), 555 (0.86x10$^4$), 609 (0.18x10$^4$), 1950 (0.08x10$^4$) nm.

**Elemental analysis** ($C_{26}H_{34}CuN_{12}PF_{6}$, $MW$: 723.15 g mol$^{-1}$):

calcd. C 43.18, H 4.74, N 23.24; found C 43.09, H 5.17, N 22.82.

[Cu(L2)2]SbF$_6$ [Cu(L2)2] (46.6 mg, 0.08 mmol, 1 eq.) and AgSbF$_6$ (28 mg, 0.08 mmol, 1.02 eq.) were treated with CH$_2$Cl$_2$ (3 ml). The deep purple reaction mixture was stirred for 23 h and filtered under argon. The solvent was removed *in vacuo* and the residue was washed with Et$_2$O (2x3 ml). The crude product was obtained as a dark powder. Crystals suitable for XRD analysis were obtained by dissolving the product in 1,2-difluorobenzene and layering the solution with *n*-pentane.

[Cu(L2)2]PF$_6$ [Cu(L2)2] (64 mg, 0.11 mmol, 1 eq.) was dissolved in CH$_2$Cl$_2$ (3 ml). FcPF$_6$ (36.3 mg, 0.11 mmol, 1 eq.) was added, resulting in a deep purple reaction mixture which was stirred for 20 h. The solvent was removed *in vacuo* and the residue was washed with Et$_2$O (4x3 ml) and Hexane (3 ml). The product was obtained as a dark powder (60 mg, 0.082 mmol, 75 %).

**Paramagnetic $^1$H NMR** (399.89 MHz, CD$_2$Cl$_2$, 298.2 K): $\delta = 38.6$ (s, 4 H, CH$_2$), 35.9 (s, 4 H, CH$_2$), 23.6 (s, 12 H, NCH$_3$), 19.1 (s, 2 H, CH$_{arom.}$), 12.0 (s, 2 H, CH$_{arom.}$), $-18.4$ (s, 2 H, CH$_{arom.}$), $-28.0$ (s, 2 H, CH$_{arom.}$) ppm.

**UV-vis** (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε in L mol$^{-1}$ cm$^{-1}$) = 230 (3.36x10$^4$), 318 (1.96x10$^4$), 353 (2.39x10$^4$), 485 (0.78x10$^4$), 720 (0.37x10$^4$), 1950 (0.03x10$^4$) nm.

**Elemental analysis** ($C_{24}H_{26}CuN_{10}S_{2}PF_{6}$, $MW$: 729.19 g mol$^{-1}$):
calcd. C 39.53, H 3.87, N 19.21; found C 39.68, H 4.20, N 18.73.

Twofold-oxidised complexes

[Cu(L1)2](PF6)2 [Cu(L1)2] (100.0 mg, 0.17 mmol, 1 eq.) and FcPF6 (106 mg, 0.32 mmol, 1.85 eq.) were treated with CH2Cl2 (5 ml). The deep purple reaction mixture was stirred for 17h and subsequently the solvent was removed in vacuo and the residue was washed with Et2O (8x3 ml). A small amount of crystals suitable for XRD analysis were grown by dissolving the product in acetone and layering the solution with n-pentane.

[Cu(L1)2](SbF6)2 [Cu(L1)2] (31.2 mg, 0.05 mmol, 1 eq.) and AgSbF6 (37.0 mg, 0.11 mmol, 2 eq.) were treated with CH2Cl2 (3 ml). The deep purple reaction mixture was stirred for 23 h and filtered under argon. The solvent was removed in vacuo and the residue was washed with Et2O (2x3 ml). Then, the crude product was dissolved in CHCl3 (1.5 ml) and precipitated with Et2O (8 ml). The supernatant was discarded and the precipitate was washed with Et2O (2x3 ml). The product was obtained as a dark brownish powder (33 mg, 58 %, 0.03 mmol). Crystals were obtained by slow solvent evaporation from a saturated DCM solution of [Cu(L1)2](SbF6)2.

UV-vis (CH2Cl2): \( \lambda_{\text{max}} (\varepsilon \text{ in L mol}^{-1} \text{ cm}^{-1}) = 231 \ (2.85 \times 10^4), 344 \ (1.68 \times 10^4), 353 \ (2.39 \times 10^4), 471 \ (1.54 \times 10^4), 568 \ (1.07 \times 10^4), 1200 \ (0.20 \times 10^4) \text{ nm.} \)

Elemental analysis (C26H34CuN12Sb2F12, \( MW: 1049.69 \text{ g mol}^{-1} \)):
calcd. C 29.75, H 3.26, N 16.01; found C 29.64, H 3.45, N 15.24.

[1] B. O. BUCKMAN, J. MA, J. B. NICHOLAS, M. ADLER, K. EMAYAN, S. YUAN (BLADE THERAPEUTICS INC), WO2018064119A1, 2018
[2] M. Werr, E. Kaifer, H. Wadepohl, H.-J. Himmel, Chem. Eur. J. 2019, 25, 12981.
3. Analytical Data

3.1. NMR spectra

Figure S1: $^1$H NMR spectrum (600 MHz, 293.3 K, CD$_2$Cl$_2$) of HL1.

Figure S2: $^{13}$C($^1$H) NMR spectrum (150.93 MHz, 295.1 K, CD$_2$Cl$_2$) of HL1.
**Figure S3:** $^1$H NMR spectrum (600 MHz, 295 K, CD$_2$Cl$_2$) of HL2, traces of 1,3-dimethyl-2-imidazolidinon (DMEU).

**Figure S4:** $^{13}$C($^1$H) NMR spectrum (150.93 MHz, 295 K, CD$_2$Cl$_2$) of HL2, traces of 1,3-Dimethyl-2-imidazolidinon (DMEU).
Figure S5: $^1$H NMR spectrum (399.89 MHz, 295.2 K, CD$_2$Cl$_2$) of [Zn(L1)$_2$].

Figure S6: $^{13}$C($^1$H) NMR spectrum (100.56 MHz, 295.2 K CD$_2$Cl$_2$) of [Zn(L1)$_2$].
3.2. Paramagnetic NMR

**Theoretical Background – magnetic coupled systems:**

An organic radical is often not detectable by NMR due to slow relaxation processes. For a paramagnetic substance, the spin lattice relaxation (T₁) is usually governed by the relaxation through coupling with the unpaired electron and therefore by the electron spin lattice relaxation time (T₁e). Organic radicals have slow electron-spin lattice relaxation (long T₁e) and therefore are usually not detectable by NMR but EPR. However, the presence of a (paramagnetic) metal (that carries some degree of electron spin), can lead to more effective and therefore faster relaxation resulting in shorter T₁e. If the relaxation is fast enough, reasonable sharp signals in both the ¹H and ¹³C NMR spectra can be observed.

The NMR chemical shift δ_{Obs,T} for paramagnetic substances can be expressed as the sum of a “diamagnetic” shift (orbital term δ_{Orb,T} independent) and a “paramagnetic” shift (δ_{HF,T} hyperfine term, temperature-dependent). The hyperfine term itself consists of the through-bond Fermi contact (δ_{FC,T}) and the through-space pseudo contact (δ_{PC,T}) term. If the pseudo contact exchange is small, the chemical shift of the paramagnetic contribution is governed by the Fermi contact shift:

\[ \delta_{obs,T} = \delta_{orb} + \delta_{con,T} \equiv \delta_{orb} + \delta_{FC,T} + \delta_{PC,T} \quad \text{for } \delta_{FC,T} \gg \delta_{PC,T} \quad \delta_{obs,T} = \delta_{orb} + \delta_{FC,T} \]

In the absence of special interactions, the Fermi contact shift has a 1/T dependency (Curie behaviour):

\[ \delta_{FC,T} = \frac{10^6 \cdot g_e \mu_B}{3\gamma_{Nuc}k_BT} S(S+1) \]

Where \( g_e \) is the free electron g-factor, \( \mu_B \) is the Bohr magneton, \( k_B \) is the Boltzmann constant, \( S \) is the spin quantum number of the d-metal center (or organic radical), \( \gamma_{Nuc} \) is the gyromagnetic ratio, \( A \) is the isotropic hyperfine coupling constant of the measured NMR nucleus (in Hz) and the factor \( 10^6 \) is present for the conversion of the into ppm.

However, the hyperfine shift and electron relaxation are affected by magnetically coupled electrons. The Hamiltonian describing the magnetic coupling in a binuclear system can be expressed with the following equation:

\[ H = -J S_1 S_2 \quad \text{(S1)} \]

Where \( J \) is the isotropic exchange coupling constant and \( S_1 \) and \( S_2 \) are local spin operators for each source of unpaired electrons (metal center or π-radical). The equation for the energies of the total spin states is then:

\[ E(S') = -\frac{1}{2} S'(S' + 1) \quad \text{(S2)} \]

Where \( S' \) is the total spin quantum number for the coupled system, which reaches from \( |S_1 + S_2| \) to \( |S_1 - S_2| \) (\( S_1 \) and \( S_2 \) are the corresponding spin quantum numbers of the individual metal centres/ radicals). Using this Hamiltonian, a positive \( J \) value describes a ferromagnetic coupling, and a negative \( J \) value describes antiferromagnetic coupled system. The expression which correlates the experimental Fermi-contact shift value with the energy of the sublevels (and, thus, with \( J \)) is given by the following equation:

\[ \delta_{FC,T} = \frac{10^6 \cdot g_e \mu_B}{3\gamma_{Nuc}k_BT} \cdot \sum_j \frac{A_j \sum_i C_{ij} S'_i (S'_i + 1) (2S'_i + 1) \exp(-E_i/k_BT)}{\sum_{i}(2S'_i + 1) \exp(-E_i/k_BT)} \quad \text{(S3)} \]

Where \( \delta_{FC,T} \) is the experimental, temperature dependent Fermi-contact shift of the dimer, \( i \) denotes the energy levels, \( j \) denotes the metal center/radical, \( A_j \) are the hyperfine couplings of the monomers (i.e. due to only one source of unpaired electrons) and \( 10^6 \) is the conversion factor to ppm. \( C_{ij} \) are spin projection coefficients for every source of unpaired electrons and for each \( ij \) total spin state, which can be calculated with the following equation:

\[ C_{i1} = [S'_i (S'_i + 1) + S_1 (S_1 + 1) - S_2 (S_2 + 1)]/[2S'_i (S'_i + 1)] \quad \text{(S4)} \]
\[ C_{i2} = \frac{[S'_{i} (S'_{i} + 1) + S_2 (S_2 + 1) - S_1 (S_1 + 1)]}{[2S'_{i} (S'_{i} + 1)]} \]  

(S5)

These constants indicate how much each \( S_i \) is contributing to the wave function of the magnetically coupled system, and may have either positive or negative values, so that the sum of these constants for each individual energy level equals one. \( \gamma_{\text{nuc}} \) (in MHz/T) is the gyromagnetic ratio for the observed nucleus (i.e. \(^1\)H and \(^{13}\)C) all other symbols have their usual meanings. The \( \delta_{FC,T,i} \) terms can be directly obtained by fitting the NMR data, or approximated from DFT calculations of monomer complexes. In the case of the oxidised complexes \([\text{Cu(L1)}_2]\text{PF}_6\) and \([\text{Cu(L2)}_2]\text{PF}_6\), \( S_i = S_2 = \frac{1}{2} \), the relative energies of the total spin states (from eq. S2) are zero (\( E_i, S' = 0 \)) and \(-J (E_2, S' = 1) \). From equations S4 and S5, it follows that \( C_{21} = C_{22} = \frac{1}{2} \) and \( C_{11} = C_{12} = 0 \). Thus, one obtains a form of equation S6 which is applicable and convenient for fitting the experimental Fermi-contact shift \( \delta_{FC,T} \) values of \([\text{Cu(L1)}_2]\text{PF}_6\) and \([\text{Cu(L2)}_2]\text{PF}_6\) estimated from the observed shift \( \delta_{\text{obs},T} \) and the diamagnetic contributions \( \delta_{\text{orb}} \) derived from the diamagnetic \([\text{Zn(L1)}_2]\) complex:[S2a]

\[ \delta_{FC,T} = 10^6 \cdot \frac{g_{eB}}{3\gamma_{\text{nuc}}k_B T} \cdot A \frac{3 \exp \left( \frac{-E_2/k_B T}{1 + 3 \exp \left( \frac{-E_2/k_B T}{T} \right)} \right)}{1 + 3 \exp \left( \frac{-E_2/k_B T}{T} \right)} \]  

(S6)

Therefore, the experimental data can be fitted with the following formulas for \(^1\)H or \(^{13}\)C NMR data, which includes the interconversion \( J \) in cm\(^{-1}\) and \( k_B \):

\[ \delta_{FC}(1H) = 10^6 \cdot \frac{1.052983 \times 10^{-2} \text{K/MHz}^{-1}}{T} \cdot A \frac{3 \exp \left( \frac{1.43867 \times J}{T} \right)}{1 + 3 \exp \left( \frac{1.43867 \times J}{T} \right)} \]

\[ \delta_{FC}(13C) = 10^6 \cdot \frac{4.18802 \times 10^{-2} \text{K/MHz}^{-1}}{T} \cdot A \frac{3 \exp \left( \frac{1.43867 \times J}{T} \right)}{1 + 3 \exp \left( \frac{1.43867 \times J}{T} \right)} \]

with \( T \) in K, \( A \) in MHz and \( J \) in cm\(^{-1}\).

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[S1] M. Enders Assigning and Understanding NMR Shifts of Paramagnetic Metal Complexes. In Modelling of Molecular Properties, Ed. P. Comba, Wiley-VCH: Weinheim, Germany, 2011

[S2] a) M. Knaupp, F.H. Köhler, Coord. Chem. Rev. 2009, 253, 2376; b) J. Vaara, Can. J. Chem. 2009, 954.

[S3] a) I.Bertini, C. Luchinat, Coord. Chem. Rev. 1996, 150, 131; b) L. Banci, I. Bertini; C. Luchinat, The 1H NMR parameters of magnetically coupled dimers – The Fe2S2 proteins as an example. In Bioorganic Chemistry. Springer Berlin-Heidelberg: Germany, 1990; Vol. 72, pp 113–136; c) H. Hillbig, P. Hudeczek, F.H. Köhler, X. Xie, P. Bergerat, O. Kahn, Inorg. Chem. 1998, 37, 4246; d) H. Hillbig, F.H. Köhler, New J. Chem. 2001, 25, 1152; e) P.W. Kopf, R.W. Kreilick, J. Am. Chem. Soc. 1969, 91, 6569; f) G.N. La Mar, NMR of Paramagnetic Molecules: Principles and Applications. Academic Press, INC.: New York and London, 1973; g) T.E. Machonkin, W.M. Westler, J.L. Markley, Inorg. Chem. 2005, 44, 779; h) C.E. Kriley, P.E. Fanwick, I.P. Rothwell, J. Am. Chem. Soc. 1994, 116, 5225; i) F. Paul, A. Bondon, G. da Costa, F. Malvolti, S. Sinbandhit, O. Cador, K. Costuas, L. Toupet, M.-L. Boillot, Inorg. Chem. 2009, 48, 10608; j) j) I. Bertini, C. Luchinat, G. Parigi, E. Ravera, Chapter 11 – Magnetically coupled systems in NMR of Paramagnetic Molecules (Second Ed.) Elsevier, 2017, 347-381.
Figure S7: Variable temperature paramagnetic $^1$H NMR spectra of [Cu(L1)$_2$]PF$_6$ (399.89 MHz) in CD$_2$Cl$_2$ traces of Fc (4.05 ppm).

Figure S8: Variable temperature paramagnetic $^1$H NMR spectra of [Cu(L1)$_2$]PF$_6$ (399.89 MHz) in CD$_2$Cl$_2$ detail enlargement for the CH$_2$ signal and its behaviour at lower temperatures.
Table S1: Calculated $^1$H NMR shift $\delta_{\text{con}}$ (in ppm) of [Cu(L1)$_2$]PF$_6$ in CD$_2$Cl$_2$ at variable temperature from the observed chemical shift $\delta_{\text{Obs}}$ and the diamagnetic contribution $\delta_{\text{Orb}}$ from [Zn(L1)$_2$].

| Assignment | CHa | CHb | CHc | CHd | CH3 | CH3 | CH2* |
|------------|-----|-----|-----|-----|-----|-----|------|
|            | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ |
| 308.69     | 3.56 | -18.61 | -52.14 | -81.95 | 64.88 | 63.24 | 105.69 |
| 298.26     | 3.80 | -18.48 | -52.44 | -82.26 | 64.79 | 62.85 | 105.76 |
| 288.18     | 4.06 | -18.20 | -52.34 | -81.91 | 64.26 | 62.03 | 105.27 |
| 277.96     | 4.29 | -17.80 | -51.90 | -81.05 | 63.31 | 60.81 | 104.16 |
| 268.34     | 4.51 | -17.23 | -51.02 | -79.46 | 61.76 | 59.00 | 102.34 |
| 258.13     | 4.69 | -16.50 | -49.67 | -77.13 | 59.70 | 56.72 | 99.05 |
| 247.60     | 4.82 | -15.62 | -47.86 | -74.13 | 56.94 | 53.76 | 94.94 |
| 238.29     | 4.90 | -14.73 | -45.87 | -70.85 | 54.20 | 50.88 | 90.73 |
| 229.65     | 4.93 | -13.62 | -43.25 | -66.58 | 50.63 | 47.23 | 84.65 |
| 219.10     | 4.92 | -12.39 | -40.22 | -61.65 | 46.60 | 43.18 | 79.49 |
| 209.73     | 4.84 | -11.19 | -37.11 | -56.64 | 42.56 | 39.18 | 72.44 |
| 199.53     | 4.70 | -10.01 | -33.92 | -51.53 | 38.48 | 35.19 | 66.50 |

*Signal splits up at low temperatures, in this cases the averaged value was used

Table S2: Estimated $^1$H $\delta_{\text{Orb}}$ from [Zn(L1)$_2$] (399.89 MHz, CD$_2$Cl$_2$, 295 K) Note that for 1-4, 10-13 the exact proton is not distinguishable.

| Assignment | $\delta_{\text{Orb}}$/ppm |
|------------|--------------------------|
| 1          | 6.74-6.66                |
| 2          | 6.74-6.66                |
| 3          | 6.74-6.66                |
| 4          | 6.74-6.66                |
| 7          | 3.33                     |
| 10         | 3.42                     |
| 11         | 2.61                     |
| 12         | 3.31/3.20                |
| 13         | 3.31/3.20                |
**Figure S9:** Plot of the $\delta_{\text{con}}^1$H NMR data for [Cu(L1)$_2$]PF$_6$ versus temperature (T). The black lines indicate the data obtained by fitting the experimental data with equation S6. For each of the $^1$H signals $J$ and $A$ were fitted, then the $J$ value was averaged (except for Signal CHa, which deviated due to the low contribution of $\delta_{\text{con}}$) and the plots were fitted with constant $J$ of $-451.2$ cm$^{-1}$ results are given in Table S4.

**Table S3:** Fit results of the $\delta_{\text{con}}^1$H NMR data for [Cu(L1)$_2$]PF$_6$. Estimation of the hyperfine coupling constants $A$ with an averaged $J = -451.2$ cm$^{-1}$.

|       | CHa   | CHb    | CHc    | CHd    | CH3   | CH3    | CH2    |
|-------|-------|--------|--------|--------|-------|--------|--------|
| $A$ / MHz | $(0.57 \pm 0.04)$ | $-2.03 \pm 0.02$ | $-6.09 \pm 0.06$ | $-9.45 \pm 0.07$ | $7.32 \pm 0.05$ | $6.96 \pm 0.06$ | $12.14 \pm 0.09$ |
Figure S10: $^1$H COSY NMR spectrum (600.20 MHz, 293.1 K, CD$_2$Cl$_2$) of [Cu(L1)$_2$]PF$_6$ showing spin-spin coupling between the aromatic protons at 10.79 ppm (291.2 K) and -11.62ppm (291.2 K).
**[Cu(L1)]_{2}PF_{6} – ^{13}C NMR spectra**

**Figure S11:** $^{13}C\{^1H\}$ NMR (150.92 MHz) of [Cu(L1)]_{2}PF_{6} at 293.1 K.

**Figure S12:** Variable temperature paramagnetic $^{13}C\{^1H\}$ NMR of [Cu(L1)]_{2}PF_{6} (150.92 MHz) in CD_{2}Cl_{2} traces of Fc (67.79 ppm). Not that only signal D was assignable as an aromatic CH.
Figure S13: $^1$H-$^{13}$C HETCOR NMR experiment for [Cu(L1)$_2$]PF$_6$ (150.92 MHz, 293.1K) in CD$_2$Cl$_2$ showing correlation between an aromatic proton (CH$_b$, -11.69 ppm) and the connected carbon D (-33.9 ppm). Note that only signal D was assignable as an aromatic CH.

Table S4: Calculated $^{13}$C NMR shift $\delta_{con}$ (in ppm) of [Cu(L1)$_2$]PF$_6$ in CD$_2$Cl$_2$ at variable temperature from the observed chemical shift $\delta_{Obs}$ and the diamagnetic contribution $\delta_{Orb}$ from Zn(L1)$_2$. Note that only signal D was assignable as an aromatic CH.

| T/K    | $\delta_{con}$ | $\delta_{Obs}$ | $\delta_{Obs}$ | $\delta_{Obs}$ | $\delta_{Obs}$ | $\delta_{Obs}$ | $\delta_{Obs}$ | $\delta_{Obs}$ |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 309.98 | -145.0         | 451.1          | 311.7          | 228.6          | -94.2          | -134.1         | -143.6         | -222.7         |
| 300.49 | -146.6         | 476.2          | 314.0          | 233.3          | -94.7          | -134.7         | -144.8         | -223.2         |
| 291.28 | -147.1         | 475.4          | 315.1          | 237.8          | -94.3          | -133.9         | -144.6         | -219.2         |
| 281.45 | -146.8         | 470.5          | 315.0          | 242.3          | -92.9          | -131.8         | -143.2         | -212.6         |
| 271.56 | -145.5         | 467.2          | 313.5          | 245.8          | -90.5          | -128.6         | -139.5         | -203.9         |
| 261.58 | -143.3         | 458.8          | 310.5          | 248.9          | -87.3          | -124.0         | -134.1         | -191.6         |
| 251.64 | -139.8         | 447.9          | 305.5          | 250.9          | -82.4          | -118.1         | -126.3         | -175.8         |
| 240.93 | -134.5         | 433.4          | 298.9          | 251.9          | -76.0          | -110.4         | -115.9         | -156.3         |
| 235.98 | -131.3         | 424.8          | 294.8          | 251.8          | -72.4          | -106.4         | -109.9         | -144.9         |
| 232.82 | -128.7         | 418.1          | 291.5          | 251.6          | -69.7          | -102.6         | -102.6         | -136.7         |
Table S5: Estimated $^{13}$C NMR shift $\delta_{\text{obs}}$ from $[\text{Zn(L1)}_2]$ (399.89 MHz, CD$_2$Cl$_2$, 295 K). Note that for 1-4, 5-6, 8-13 the exact carbon is not distinguishable.

| assignment | $\delta_{\text{obs}}$ | comment | av.value |
|------------|----------------|--------|----------|
| 1          | 119.64        | CH     |          |
| 2          | 117.5         | CH     |          |
| 3          | 109.59        | CH     | 112.9    |
| 4          | 104.7         | CH     |          |
| 5          | 140.8         | CqArom | 139.2    |
| 6          | 137.7         | CqArom |          |
| 7          | 36.3          | CH3    |          |
| 8          | 160.5         | CqGua  |          |
| 9          | 160.2         | CqGua  |          |
| 10         | 38.6          | CH3a   | 33.2     |
| 11         | 27.8          | CH3b   |          |
| 12         | 51.2          | CH2    | 50.9     |
| 13         | 50.5          | CH2    |          |

Figure S14: Plot of the $\delta_{\text{con}}$ $^{13}$C NMR data of signal D for $[\text{Cu(L1)}_2]\text{PF}_6$ versus temperature (T). No satisfying fit was obtained. The red line results from a fit of the experimental data with equation S6 and $A = -3.15$ MHz and $J = -372.0$ cm$^{-1}$. 
Figure S15: Variable temperature paramagnetic $^1$H NMR spectra of [Cu(L2)$_2$]PF$_6$ (399.89 MHz) in CD$_2$Cl$_2$ traces of Fc (4.15 ppm).
Figure S16: $^1$H NOESY spectrum (CD$_2$Cl$_2$, 600.20 MHz) of [Cu(L2)$_2$]PF$_6$ for the two downfield shifted signals showing chemical exchange (in phase positive signal) mixing time 0.1 sec.

Table S6: Calculated 1H NMR shift $\delta_{\text{con}}$ (in ppm) of [Cu(L2)$_2$]PF$_6$ in CD$_2$Cl$_2$ at variable temperature from the observed chemical shift $\delta_{\text{Obs}}$ and the diamagnetic contribution $\delta_{\text{Orb}}$ from [Zn(L1)$_2$] (see Table S2).

| T/K   | ChA | ChB | ChC | ChD | Ch3 | Ch2a | Ch2b |
|-------|-----|-----|-----|-----|-----|------|------|
|       | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ |
| 308.69 | 13.75 | 5.85 | -28.21 | -39.09 | 23.12 | 39.38 | 36.71 |
| 298.26 | 12.40 | 5.26 | -25.13 | -34.70 | 20.59 | 35.32 | 32.69 |
| 288.18 | 11.09 | 4.69 | -22.13 | -30.42 | 18.13 | 31.36 | 28.82 |
| 277.96 | 9.77  | 4.13 | -19.16 | -26.20 | 15.68 | 27.35 | 24.96 |
| 268.34 | 8.47  | 3.57 | -16.27 | -22.08 | 13.28 | 23.38 | 21.20 |
| 258.13 | 7.30  | 3.09 | -13.73 | -18.47 | 11.15 | 19.84 | 17.90 |
| 247.60 | 6.20  | 2.63 | -11.3 | -15.01 | 9.12  | 16.43 | 14.74 |
| 238.29 | 5.33  | 2.26 | -9.41  | -12.33 | 7.53  | 13.72 | 12.25 |
| 229.65 | 4.05  | 1.93 | -7.62  | -9.80  | 6.02  | 11.13 | 9.91  |
| 219.10 | 3.74  | 1.62 | -6.01  | -7.49  | 4.64  | 8.74  | 7.77  |
| 209.73 | 3.16  | 1.39 | -4.77  | -5.72  | 3.58  | 6.89  | 6.12  |
| 199.53 | 2.65  | 1.19 | -3.70  | -4.21  | 2.65  | 5.26  | 4.64  |
Figure S17: Plot of the $\delta_{\text{con}}$ $^1$H NMR data for [Cu(L2)$_2$]PF$_6$ versus temperature (T). The black lines indicate the data obtained by fitting the experimental data with equation S6. For each of the $^1$H signals $J$ and $A$ were fitted, then the $J$ value was averaged and the plots were fitted with constant $J$ of -976.33 cm$^{-1}$ results are given in Table S7.

Table S7: Fit results of the $\delta_{\text{con}}$ $^1$H NMR data for [Cu(L2)$_2$]PF$_6$. Estimation of the hyperfine coupling constants $A$ with an averaged $J = -976.33$ cm$^{-1}$.

|      | CHa       | CHb       | CHc       | CHd       | CH3       | CH2a      | CH2b      |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| A / MHz | $13.64 \pm 0.21$ | $5.79 \pm 0.10$ | $-26.73 \pm 0.13$ | $-36.49 \pm 0.42$ | $21.79 \pm 0.18$ | $37.91 \pm 0.10$ | $34.79 \pm 0.17$ |
Figure S18: $^{13}$C NMR spectrum ($^1$H coupled) (150.92 MHz) of [Cu(L2)$_2$]PF$_6$ at 293.0 K.

Figure S19: Variable temperature paramagnetic $^{13}$C NMR spectra of [Cu(L2)$_2$]PF$_6$ (399.89 MHz) in CD$_2$Cl$_2$. Assignment via $^1$H,$^{13}$C-HSQC experiment (see Figure S20). Note Signals A, B, C could not be assigned.
Figure S20: Low temperature $^1$H-$^{13}$C-HSQC NMR experiment of [Cu(L2)$_2$]PF$_6$ (600.18 MHz, 232.82 K) in CD$_2$Cl$_2$ for assignment of the $^{13}$C Signals. Note signals A, B, C from the $^{13}$C spectra could not be assigned.
Table S8: Calculated $^{13}$C NMR shift $\delta_{\text{con}}$ (in ppm) of [Cu(L2)$_2$]PF$_6$ in CD$_2$Cl$_2$ at variable temperature from the observed chemical shift $\delta_{\text{Obs}}$ and the diamagnetic contribution $\delta_{\text{Orb}}$ from [Zn(L1)$_2$] (see Table S5). Note signals A, B, C could not be assigned.

| assignment | CHa | CHb | CHc | CHd | CH2 | CH3 |
|------------|-----|-----|-----|-----|-----|-----|
| T / K      | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ | $\delta_{\text{con}}$ |
| 309.98     | 229.4 | 157.8 | -135.8 | -178.3 | -54.3 | -37.7 |
| 300.49     | 206.6 | 142.4 | -120.7 | -159.0 | -48.9 | -34.1 |
| 291.28     | 184.6 | 126.6 | -103.9 | -139.4 | -43.6 | -30.5 |
| 281.45     | 161.6 | 110.9 | -90.2 | -120.0 | -38.5 | -26.7 |
| 271.56     | 139.8 | 96.2 | -75.6 | -101.3 | -33.6 | -23.0 |
| 261.58     | 119.4 | 81.6 | -61.5 | -83.8 | -28.8 | -19.4 |
| 251.64     | 100.9 | 68.8 | -49.1 | -67.7 | -24.5 | -16.2 |
| 240.93     | 84.4 | 57.1 | -37.8 | -53.5 | -20.6 | -13.2 |
| 235.98     | 76.8 | 51.7 | -32.6 | -47.0 | -18.9 | -11.8 |
| 232.82     | 71.2 | 47.8 | -28.9 | -42.2 | -17.6 | -10.8 |

Figure S21: Plot of the $\delta_{\text{con}}$ $^{13}$C NMR data for [Cu(L2)$_2$]PF$_6$ versus temperature (T). The black lines indicate the data obtained by fitting the experimental data with equation S6. For each of the $^1$H signals $J$ and $A$ were fitted, then the $J$ value was averaged, and the plots were fitted again with a constant $J$ of -1026.3 cm$^{-1}$. The resulting $A$ values are collected in Table S9.

Table S9: Fit results of the $\delta_{\text{con}}$ $^{13}$C NMR data for [Cu(L2)$_2$]PF$_6$. Estimation of the hyperfine coupling constants $A$ with an averaged $J = -1026.3$ cm$^{-1}$. The resulting $A$ values are extraordinary large.

| A / MHz | CHa | CHb | CHc | CHd | CH2 | CH3 |
|---------|-----|-----|-----|-----|-----|-----|
| -       | 69.67 ± 0.62 | 47.79 ± 0.34 | -38.66 ± 0.75 | -51.64 ± 0.64 | -16.61 ± 0.21 | -11.40 ± 0.05 |
Scheme S1. Illustration of the dynamic processes I and II in [Cu(L1)₂]^+ and [Cu(L2)₂]^+ which is observed in the temperature dependent ^1H NMR spectra Figure SX and Figure SX and discussed in the main part.
3.3. UV-vis-NIR Spectra

**Figure S22:** UV-vis-NIR spectrum (CH$_2$Cl$_2$) of [Cu(L1)$_2$] (c = 1.48x10$^{-5}$ mol/l). The inlet shows the spectrum for a higher concentration (c = 5.19x10$^{-4}$ mol/l).

**Figure S23:** UV-vis-NIR spectrum (CH$_2$Cl$_2$) of [Cu(L2)$_2$] (c = 1.83x10$^{-5}$ mol/l). The inlet shows the spectrum for a higher concentration (c = 3.35x10$^{-4}$ mol/l)
**Figure S24**: UV-vis-NIR spectrum (CH$_2$Cl$_2$) of [Cu(L1)$_2$]PF$_6$ (c = $3.97 \times 10^{-5}$ mol/l, inlet c = $6.68 \times 10^{-4}$ mol/l). The Inlet shows the spectrum for a higher concentration, zooming into the NIR region.

**Figure S25**: UV-vis-NIR spectrum (CH$_2$Cl$_2$) of [Cu(L2)$_2$]PF$_6$ (c = $4.23 \times 10^{-5}$ mol/l, inlet c = $1.64 \times 10^{-4}$ mol/l). The Inlet shows the spectrum at a higher concentration, zooming into the NIR region.
Figure S26: UV-vis-NIR spectrum (CH$_2$Cl$_2$) of [Cu(L1)$_2$(SbF$_6$)$_2$] (c = 5.99x10$^{-5}$ mol/l).

Figure S27: UV-vis spectrum (CH$_2$Cl$_2$) of [Zn(L1)$_2$] (c = 1.94x10$^{-5}$ mol/l). No bands were observed in the NIR region (up to 2500 nm).
Figure S28: UV-vis spectrum of \([\text{Cu}(L_1)_2]\) \((1.48 \times 10^{-5} \text{ mol/l})\) in \(\text{CH}_2\text{Cl}_2\) together with a TD-DFT simulation of the electronic excitations (Lorentzian broadening StdDev = 1200, calculated spectrum shifted 1200 cm\(^{-1}\) to fit the lowest energy transition) of \([\text{Cu}(L_1)_2]\). Visualisation of the major contributions to three lowest energy transitions (isoval. 0.05).

Figure S29: UV-vis spectrum of \([\text{Cu}(L_2)_2]\) \((1.84 \times 10^{-5} \text{ mol/l})\) in \(\text{CH}_2\text{Cl}_2\) together with a TD-DFT simulation of the electronic excitations (Lorentzian broadening StdDev = 1200, Spectrum shifted 860 cm\(^{-1}\) to fit the lowest energy transition) of \([\text{Cu}(L_2)_2]\). Visualisation of the major contribution to the lowest energy transition (isoval. 0.05).
3.4. Cyclic voltammetry (CV) measurements

Figure S30: Cyclic voltammetry (CV) curves of compounds HL1 and HL2 in CH₂Cl₂ (Ag/AgCl reference electrode, 0.1 M (nBu)₄(PF₆) as supporting electrolyte, scan rate 100 mV s⁻¹). Potentials given vs. the Fc⁺/Fc redox couple.

|       | E₁/₂  | ΔE  |
|-------|-------|-----|
| HL1   |       |     |
| Eᵣᵣ   | -0.545 | -0.49 | 0.103 |
| Eₓₓ   | -0.442 |       |     |
| HL2   |       |     |
| Eᵣᵣ   | -0.366 | -0.30 | 0.132 |
| Eₓₓ   | -0.235 |       |     |
Figure S31: Cyclic voltammetry curve for HL1, measured with variable scan speed (vs. Ag/AgCl, 0.1 M \( \text{N}(n\text{Bu})_4(\text{PF}_6) \), CH\(_2\)Cl\(_2\)).

Figure S32: Cyclic voltammetry curve for HL2, measured with variable scan speed (vs. Ag/AgCl, 0.1 M \( \text{N}(n\text{Bu})_4(\text{PF}_6) \), CH\(_2\)Cl\(_2\)).
Figure S33: Cyclic voltammetry (CV) curves for [Cu(L1)₂] and [Cu(L2)₂] in CH₂Cl₂ (Ag/AgCl reference electrode, 0.1 M N(nBu)₄(PF₆) as supporting electrolyte, scan rate 100 mV s⁻¹). Potentials given vs. the Fc⁺/Fc redox couple.

Potentials (in V, vs. Fc⁺/Fc) observed in the cyclic voltammograms of [Cu(L1)₂] and [Cu(L2)₂] in CH₂Cl₂.

|                  | [Cu(L1)₂]       | [Cu(L2)₂]       |
|------------------|-----------------|-----------------|
| E_{1/2}(1) / E_{ox}(1) | -1.40 / -1.31   | -1.29 / -1.36   |
| E_{1/2}(2) / E_{ox}(2) | -0.71 / -0.65   | -0.44 / -0.38   |
| E_{1/2}(3) / E_{ox}(3) | -0.27 / -0.21   | -0.03⁻ / +0.05  |
| E_{1/2}(4) / E_{ox}(4) | +0.09 / +0.15   | +0.31 / +0.38   |

*Waves broaden with increasing scan speed, especially in direction of reduction.*
Figure S34: Cyclic voltammetry curve for \([\text{Cu}(L1)_2]\), measured with variable scan speed (vs. Ag/AgCl, 0.1 M \(\text{N}(\text{nBu})_4(\text{PF}_6)\), CH\(_2\)Cl\(_2\)).

Figure S35: Cyclic voltammetry curve for \([\text{Cu}(L2)_2]\), measured with variable scan speed (vs. Ag/AgCl, 0.1 M \(\text{N}(\text{nBu})_4(\text{PF}_6)\), CH\(_2\)Cl\(_2\)).
3.5. EPR spectroscopy

Figure S36: X-band EPR spectrum of [Cu(L1)]$_2$ (frozen CH$_2$Cl$_2$ solution, 6.4 K, 9.63338 GHz, $g_\parallel = 2.174$, $g_\perp = 2.064$, $A_\parallel = 15.4$ mT).

Figure S37: X-band EPR spectrum of [Cu(L2)]$_2$ (frozen CH$_2$Cl$_2$ solution, 6.5 K, 9.632366 GHz, with $g_x$, $g_y$, $g_z$ and $A_\parallel = 14.015$ mT). The signal close to $g_x$ might be caused by a minor organic radical impurity.
Figure S38: X-Band EPR spectrum of \([\text{Cu(L1)}_2]\text{PF}_6\) (frozen \(\text{CH}_2\text{Cl}_2\) solution, 6.5 K, 9.631779 GHz).

Figure S39: X-band EPR spectrum of \([\text{Cu(L1)}_2]\text{PF}_6\) frozen \(\text{CH}_2\text{Cl}_2\) solution (6.4 K) and room-temperature \(\text{CH}_2\text{Cl}_2\) solution.
Figure S40: X-Band EPR spectrum of $[\text{Cu(L2)}_2]\text{PF}_6$ (frozen CH$_2$Cl$_2$ solution, 6.8 K, 9.632524 GHz).

Figure S41: X-band EPR spectrum of $[\text{Cu(L2)}_2]\text{PF}_6$ (frozen CH$_2$Cl$_2$ solution vs room-temperature solution).
Figure S42: X-Band EPR spectrum of [Cu(L1)2]([SbF6]2) (room-temperature solution CH2Cl2, 9.622898 GHz, g = 2.004)
3.5. SQUID measurements

Figure S43: Plot of the magnetometric (SQUID) data for [Cu(L1)$_2$(SbF$_6$)$_2$ in the temperature range 2–180 K measured at 50 mT.
3.6. XP spectra

**Figure S44:** C 1s XP spectra of the complexes $[\text{Cu}(L1)_2]\text{PF}_6$ and $[\text{Cu}(L2)_2]\text{PF}_6$ (open circles).

**Figure S45:** N 1s XP spectra of the complexes $[\text{Cu}(L1)_2]\text{PF}_6$ and $[\text{Cu}(L2)_2]\text{PF}_6$ (open circles).
Figure S46: S 2p XP spectrum of the complex and \([\text{Cu}(L2)_2]\text{PF}_6\) (open circles). The spectrum is decomposed into the 2p\(_{3/2}\) and 2p\(_{1/2}\) components, drawn in blue solid lines.
3.7. Additional information to L1H and L2H and the twofold oxidised complex

![Figure S47](image)

**Figure S47.** Illustration of the solid-state structure of hydrogen-bonded dimers of HL1. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted except for N-H. Colour code: N-blue, C-grey, H-white.

**Table S10.** Bond distances (in Å) in the four independent molecules in solid HL1.

| bond | 1     | 2     | 3     | 4     |
|------|-------|-------|-------|-------|
| a    | 1.378(2) | 1.389(2) | 1.384(2) | 1.387(2) |
| b    | 1.382(2) | 1.382(2) | 1.374(2) | 1.375(2) |
| c    | 1.295(2) | 1.295(2) | 1.295(2) | 1.296(2) |
| d    | 1.424(2) | 1.425(2) | 1.422(2) | 1.423(2) |
| e    | 1.295(2) | 1.298(2) | 1.293(2) | 1.293(2) |
| f    | 1.391(2) | 1.391(2) | 1.391(2) | 1.395(2) |
| g    | 1.391(2) | 1.388(2) | 1.395(2) | 1.393(2) |
4. Crystallographic data

4.1. Details of the structural characterisations

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Bruker D8 Venture, dual source (Mo-Kα radiation, microfocus X-ray tube, Photon III detector). Data were processed with the standard Bruker (SAINT, APEX3) software package. Multiscan absorption correction was applied using the SADABS program. The structures were solved by intrinsic phasing and refined using the SHELXTL software package (Version 2018/3). Graphical handling of the structural data during solution and refinement were performed with OLEX2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model. Hydrogen atoms bound to nitrogen were located in difference Fourier syntheses and refined, either fully or with appropriate distance and/or symmetry. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre (No. 2092838-2092844). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and details of the data collections are given in Table S11.

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[S1] SAINT (APEX III) Bruker AXS GmbH, Karlsruhe, Germany 2016.
[S2] a) G. M. Sheldrick, SADABS, Bruker AXS GmbH, Karlsruhe, Germany 2004-2014; b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, J. Appl. Cryst. 2015, 48, 3.
[S3] a) G. M. Sheldrick, SHELXT, Program for Crystal Structure Solution, University of Göttingen, Germany 2014-2018; b) G. M. Sheldrick, Acta Cryst. 2015, A71, 3.
[S4] a) G. M. Sheldrick, SHELXL-20xx, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2012-2018; b) W. Robinson, G. M. Sheldrick in: N. W. Isaaks, M. R. Taylor (eds.) „Crystallographic Computing 4“, Ch. 22, IUCr and Oxford University Press, Oxford, UK, 1988; c) G. M. Sheldrick, Acta Cryst. 2008, A64, 112; (d) G. M. Sheldrick, Acta Cryst. 2015, C71, 3.
[S5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program, J. Appl. Cryst. 2009, 42, 339.
### Table S11: Crystal data and details of the XRD data collection.

| Compound | L1H | [Cu(L1)₂] | [Cu(L2)₂] | [Zn(L1)₂] |
|----------|-----|------------|------------|-----------|
| CCDC No. | 2092840 | 2092838 | 2092843 | 2092839 |
| Formula | C₁₃H₁₈N₆ | C₂₆H₃₄CuN₁₂ | C₂₆H₳₄CuN₁₀S₂ | C₂₆H₳₄N₁₂Zn |
| \( D_{calc} \) \( g \cdot cm^{-3} \) | 1.257 | 1.423 | 1.521 | 1.415 |
| \( \mu \) \( mm^{-1} \) | 0.082 | 0.850 | 1.056 | 0.943 |
| Formula Weight | 258.33 | 578.19 | 584.22 | 580.02 |
| Colour | colourless | clear green | blue | colourless |
| Shape | plate-shaped | block-shaped | needle-shaped | block-shaped |
| Size/\( mm^3 \) | 0.30×0.28×0.13 | 0.32×0.17×0.12 | 0.17×0.05×0.05 | 0.29×0.12×0.11 |
| \( T/K \) | 100.0 | 100.0 | 100.0 | 100.0 |
| Crystal System | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space Group | \( P2_1/c \) | \( P2_1/c \) | \( Pccn \) | \( Pbcn \) |
| \( a/Å \) | 9.7180(7) | 19.634(2) | 10.5147(6) | 19.8647(10) |
| \( b/Å \) | 41.730(3) | 8.5621(9) | 12.2102(7) | 8.5969(4) |
| \( c/Å \) | 13.4729(10) | 16.0738(19) | 19.8718(12) | 15.9410(8) |
| \( \alpha/° \) | 90 | 90 | 90 | 90 |
| \( \beta/° \) | 91.948(3) | 92.564(5) | 90 | 90 |
| \( \gamma/° \) | 90 | 90 | 90 | 90 |
| \( V/Å^3 \) | 5460.5(7) | 2699.4(5) | 2551.3(3) | 2722.3(2) |
| \( Z \) | 16 | 4 | 4 | 4 |
| \( Z' \) | 4 | 1 | 0.5 | 0.5 |
| Wavelength/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Radiation type | MoKₐ | MoKₐ | MoKₐ | MoKₐ |
| \( \theta_{min} ° \) | 1.800 | 2.077 | 2.050 | 2.555 |
| \( \theta_{max} ° \) | 29.000 | 29.999 | 27.500 | 30.547 |
| Measured Refl's. | 14469 | 71322 | 62154 | 73175 |
| Indep't Refl's. | 14469 | 7857 | 2930 | 4172 |
| Refl's I≥2σ(I) | 11781 | 6028 | 2404 | 3671 |
| \( R_{int} \) | 0.0671 | 0.0668 | 0.0984 | 0.0499 |
| Parameters | 714 | 358 | 170 | 180 |
| Restraints | 0 | 0 | 0 | 0 |
| Largest Peak | 0.388 | 0.488 | 0.422 | 0.436 |
| Deepest Hole | 0.309 | -0.547 | -0.509 | -0.402 |
| GooF | 1.040 | 1.034 | 1.038 | 1.040 |
| \( wR_2 \) (all data) | 0.1432 | 0.0850 | 0.0882 | 0.0733 |
| \( wR_2 \) | 0.1328 | 0.0792 | 0.0806 | 0.0696 |
| \( R_t \) (all data) | 0.0660 | 0.0553 | 0.0445 | 0.0330 |
| \( R_t \) | 0.0520 | 0.0339 | 0.0324 | 0.0271 |
| Compound                  | [Cu(L1)₂]SbF₆ | [Cu(L2)₂]SbF₆ | [Cu(L1)₂](PF₆)₂ |
|--------------------------|----------------|----------------|----------------|
| CCDC No.                 | 2092841        | 2092844        | 2092842        |
| Formula                  | C₃₈H₄₂CuF₁₀N₁₂Sb | C₂₉H₂₆CuF₆N₁₀S₂Sb | C₂₉H₁₇CuF₁₂N₁₁OP₂ |
| D_{calc}/ g cm⁻³         | 1.665          | 1.818          | 1.595          |
| μ/mm⁻¹                   | 1.252          | 1.824          | 0.751          |
| Formula Weight           | 1042.12        | 819.97         | 926.21         |
| Colour                   | violet         | dark violet    | dull dark brown|
| Shape                    | plate-shaped   | block-shaped   | needle-shaped  |
| Size/mm³                 | 0.20×0.06×0.03 | 0.04×0.06×0.17 | 0.30×0.10×0.10 |
| T/K                      | 100.0          | 100.0          | 100.0          |
| Crystal System           | monoclinic     | monoclinic     | monoclinic     |
| Space Group              | C2/c           | P2₁/n          | P2₁           |
| a/Å                      | 25.4047(12)    | 15.915(2)      | 14.164(2)     |
| b/Å                      | 8.0251(4)      | 11.0469(14)    | 9.3074(15)    |
| c/Å                      | 21.1285(10)    | 18.340(2)      | 14.782(2)     |
| α/°                      | 90             | 90             | 90             |
| β/°                      | 105.178(2)     | 111.674(4)     | 98.237(5)     |
| γ/°                      | 90             | 90             | 90             |
| V/Å³                     | 4157.3(3)      | 2996.3(7)      | 1928.5(5)     |
| Z                        | 4              | 4              | 2              |
| Z'                       | 0.5            | 1              | 1              |
| Wavelength/Å              | 0.71073        | 0.71073        | 0.71073        |
| Radiation type           | MoKα           | MoKα           | MoKα          |
| θ_{min}/°                 | 1.997          | 2.131          | 2.151          |
| θ_{max}/°                 | 27.496         | 27.499         | 26.000         |
| Measured Refl's.         | 30442          | 100535         | 54438          |
| Indep't Refl's           | 4777           | 5888           | 7584           |
| Refl's I≥2 σ(I)          | 3310           | 5414           | 5181           |
| R_{int}                  | 0.0942         | 0.0992         | 0.1527         |
| Parameters               | 285            | 401            | 523            |
| Restraints               | 0              | 0              | 1              |
| Largest Peak             | 1.241          | 0.597          | 0.545          |
| Deepest Hole             | -0.972         | -1.003         | -0.594         |
| Goof                      | 1.033          | 1.044          | 1.016          |
| wR₂ (all data)           | 0.0905         | 0.0773         | 0.1695         |
| wR₂                      | 0.0775         | 0.0686         | 0.1395         |
| R₁ (all data)            | 0.0807         | 0.0559         | 0.1039         |
| R₁                       | 0.0442         | 0.0361         | 0.0615         |
5. Copper catalysis details

Test reactions:

\[
\text{O}_2 \quad \text{Cu/Zn cat. base} \quad \text{deuterated solv.} \quad 22 \text{ h, r.t.}
\]

In a typical aerobic alcohol oxidation experiment copper (zinc) cat (5 mol%, 10 mg) and Cs₂CO₃ (2 eq., 225 mg) were suspended in deuterated solvent (1 ml) and BzOH (1 eq, 37 µl) was added. Then the reaction mixture was bubbled with O₂ for 10 seconds and stirred for 22 h. Afterwards the reaction mixture was filtered through a syringe filter, a NMR spectrum was measured and the conversion was estimated by the ratio of BzOH and PhCHO via integration.

Table S12: Summary of the results of the catalytic experiments.

| Entry | Complex | Cat. mol% | Base | Base eq | Solvent | Substrate | Conversion/% |
|-------|---------|-----------|------|---------|---------|-----------|--------------|
| 1     | [Cu(L1)₂] | 5         | Cs₂CO₃ | 2       | CD₂Cl₂ | BzOH      | 87           |
| 2     | [Cu(L1)₂] | 1         | Cs₂CO₃ | 2       | CD₂Cl₂ | BzOH      | 62           |
| 3     | [Cu(L1)₂] | 5         | Cs₂CO₃ | 2       | Tol-d₈ | BzOH      | 93           |
| 4     | [Cu(L1)₂] | 5         | Cs₂CO₃ | 2       | CD₃CN  | BzOH      | 80           |
| 5     | [Cu(L1)₂] | 5         | Cs₂CO₃ | 1       | CD₂Cl₂ | BzOH      | 65           |
| 6     | [Cu(L1)₂] | 5         | Cs₂CO₃ | 0.1     | CD₂Cl₂ | BzOH      | 29           |
| 7     | [Cu(L1)₂] | 5         | no Base| 0       | CD₂Cl₂ | BzOH      | 29           |
| 8     | [Cu(L1)₂] | 5         | KOH   | 2       | CD₂Cl₂ | BzOH      | 10           |
| 9     | [Cu(L2)₂] | 5         | Cs₂CO₃ | 2       | CD₂Cl₂ | BzOH      | 99           |
| 10    | [Cu(L2)₂] | 2         | Cs₂CO₃ | 2       | CD₂Cl₂ | BzOH      | 98           |
| 11    | [Cu(L2)₂] | 1         | Cs₂CO₃ | 2       | CD₂Cl₂ | BzOH      | 54           |
| 12    | [Cu(L2)₂] | 5         | Cs₂CO₃ | 2       | Tol-d₈ | BzOH      | 93           |
| 13    | [Cu(L2)₂] | 5         | Cs₂CO₃ | 2       | CD₂Cl₂ | CinnOH    | 72           |
| 14    | [Cu(L2)₂] | 5         | Cs₂CO₃ | 2       | CD₂Cl₂ | nOctOH    | 2            |
| 15    | [Zn(L1)₂] | 5         | Cs₂CO₃ | 2       | Tol-d₈ | BzOH      | 17           |

*NMR conversion via substrate product ratio, assuming no side reactions

To compare the performances of [Cu(L1)₂] and [Cu(L2)₂], the conversion was followed by GC/MS analysis and the initial rate of the product formation was compared. In a flame dried and Ar purged Schlenk tube 5 mol% [Cu(L1)₂] (15 mg) or [Cu(L2)₂] (15 mg), Cs₂CO₃ (2 eq, 338 mg) and biphenyl (1 eq.) as an internal standard were suspended in CH₂Cl₂ (5 ml). Then benzyl alcohol (55 µl, 1 eq.) was added, and dioxygen was bubbled through the reaction mixture for 10 seconds, marking the starting point of the catalytic reaction. Subsequently, the reaction mixture was stirred at room-temperature. After certain time intervals, 0.2 ml of the reaction mixture were withdrawn and filtered through basic alumina before injection in the GC (alumina pipette was washed with 3 ml of EtOAc). BzOH and PhCHO were identified by coupled mass spectrometry and quantified via the internal standard. The integration of the BzOH peaks was biased by tailing of the peaks.

Figure S48 shows the plot of the concentration ratio C₂PhCHO/C₂Std as a function of the reaction time. The initial rate of product formation is similar for both complexes. After establishment of the equilibrium, we find higher conversions for the [Cu(L2)₂] complex as seen from Table S12, arguing for a higher turnover number of the [Cu(L2)₂] complex.
Figure S48: Comparison of the product formation (PhCHO) with reaction time for reactions with the catalysts [Cu(L1)$_2$] and [Cu(L2)$_2$] (5 mol% each) in the catalytic aerobic oxidation of BzOH to PhCHO, estimated by GC/MS analysis.
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