Electronic Supplementary Information

Stabilising a Quinonoid-Bridged Dicopper(I) Complex by Use of a dppf (dppf = Diphenylphosphinoferrocene) Backbone†‡

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Experimental Section

Materials and physical methods

The dppf ligand was obtained from Alfa Aesar. The quinonoid ligand **L** was synthesised according to the published procedure[i] from 4,6-diaminoresorcinol dihydrochloride which was obtained from Acros. The precursor complex, $[\{Cu(dppf)\}_2(\mu\text{-}Cl)_2]$ was prepared according to a reported procedure.[ii] All the reagents were used as supplied. The solvents used for metal complex synthesis were dried and distilled by standard techniques.

The ^1H NMR and $^{31}P\{^1H\}$ spectra, at 250.13 and 101.26 MHz respectively, were recorded on a Bruker AC 250 spectrometer. Electronic absorption studies were recorded on J&M TIDAS and Shimadzu UV 3101 PC spectrophotometers. EPR spectra in the X-band were recorded with a Bruker System EMX. Cyclic voltammetry was carried out in 0.1 M $[(n\text{-}Bu)_4N]PF_6$ solutions using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag wire as pseudo reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as internal reference. Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell. Elemental analyses were performed by the Perkin-Elmer Analyzer 240. Mass spectrometric measurements were carried out in a Bruker micrOTOF-Q spectrometer with chloroform as solvent.

Synthesis of $[\{\mathrm{Cu(dppf)}\}_2(\mu\text{-}\mathrm{L}_{-2\mathrm{H}})]$ (2).

To solid KO*t*-Bu (14 mg, 0.12 mmol) in a Schlenk flask was added 4-(*n*-butylamino)-6-(*n*-butyliminio)-3-oxocyclohexa-1,4-dien-1-olate ($\mathrm{C_6H_2(\underline{\cdots}NH}n\mathrm{\text{-}Bu)_2(\underline{\cdots}O)_2}$) **L** (30 mg, 0.12 mmol) and tetrahydrofuran (10 mL). The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure to leave an orange solid. The complex $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\kappa_2\text{-}P,P\text{-dppf})_2]$ (72 mg, 0.06 mmol) and dichloromethane (15 mL) were added and the solution was stirred for 5 h at room temperature. The solvent was removed under reduced pressure and an excess of NaH (2–3 equiv) and tetrahydrofuran (15 mL) were added. After the suspension was stirred at room temperature overnight, the tetrahydrofuran was removed and a further amount of $[\mathrm{Cu_2}(\mu\text{-Cl})_2(\kappa_2\text{-}P,P\text{-dppf})_2]$ (72 mg, 0.06 mmol) and dichloromethane (20 mL) were added. The mixture was stirred for 24 h. The end of the reaction could be checked by ^{31}P-NMR spectroscopy. The solution was filtered over Celite to remove KCl and NaCl and the dichloromethane was reduced in volume until about one-fourth was left. An excess of *n*-hexane (about 4 times) was added to the solution which was left overnight at 4 °C. The black crystals which precipitated were filtered and washed with *n*-hexane. Yield: 105 mg (60%). $\mathrm{C_{82}H_{76}N_2Cu_2Fe_2O_2P_4{\cdot}1.7(CH_2Cl_2)}$: calcd. for C 61.73, H 4.91, N 1.72%; found C 61.80, H 5.10, N 1.72%. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K) δ/ppm: 0.93 (6 H, t, J 7.3, 2 x $\mathrm{C}H_3\mathrm{(CH_2)_3N}$), 1.03–1.7 (8 H, m, 2 x $\mathrm{CH_3(C}H_2\mathrm{)_2CH_2N}$), 3.35 (4 H, m, 2 x $\mathrm{CH_3(CH_2)_2C}H_2\mathrm{N}$), 4.22 (8 H, d, br, $J_{\mathrm{P\text{-}H}}$ = 21.5 Hz, ferrocene ring *H*), 4.33 (8 H, s, br, ferrocene ring *H*), 5.17 (1 H, s, NCC*H*), 5.65 (1 H, s, OCC*H*), 7.28–7.7 (40 H, m, phenyl *H*); ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K) δ/ppm: -18.5. ES$^-$MS (m/z): 1483.22 {$[\mathbf{2}+\mathrm{H}]^+$}.

Crystallographic details

X-ray data collection, structure solution and refinement

Suitable crystals for the X-ray analysis of $\mathbf{2}{\cdot}2\mathrm{CH_2Cl_2}$ were obtained as described above. The intensity data were collected on a Kappa CCD diffractometer[iii] (graphite monochromated MoK$_\alpha$ radiation, λ = 0.71073 Å) at 173(2) K. Crystallographic and experimental details for the structure are summarized in Table S1. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[iv] with anisotropic thermal parameters for all the non-hydrogen atoms, except those mentioned below. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms.

The crystals of **2**·$2CH_2Cl_2$ were of poor quality and displayed very weak reflections at high θ values, regardless of the crystal dimensions and exposure time. After a number of attempts, the data gave a satisfactory description of the connectivity and relatively good refinement parameters.

One of the butyl groups was disordered in two positions with equal occupancy factors. These atoms were refined with restrained N-C, C-C distances and C···C angular distances. Atoms C79 and C80, together with their disordered counterparts were refined with restrained anisotropic parameters, while C81 and C82 were left isotropic with constrained thermal parameters. Some of the phenyl carbon atoms (namely: C54, C55, C66, C67, C70, C71, C72 and C73), close to the disordered parts of the structure, were refined with restrained anisotropic displacements. One of the two dichloromethane molecules was found disordered in two positions having one chloride and the carbon in common. The disordered chloride was refined with restrained anisotropic parameters.

CCDC 751134 contains the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S-1. Crystallographic and experimental details

	2·$2CH_2Cl_2$
Chemical formula	$C_{82}H_{76}Cu_2Fe_2N_2O_2P_4\cdot 2CH_2Cl_2$
M_r	1653.34
Cell setting, space group	Monoclinic, $P2_1/c$
Temperature (K)	173(2)
a, b, c (Å)	17.5376(3), 19.2134(5), 23.0786(6)
β (°)	94.991(1)
V (Å^3)	7747.0(3)
Z	4
D_x (Mg m^{-3})	1.418
Radiation type	Mo-$K\alpha$
μ (mm^{-1})	1.178
Crystal size (mm)	0.3 × 0.3 × 0.25
F(000)	3407
Meas., indep. and obsvd refl.	37998, 13787, 8645
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.199, 1.05
No. of parameters	925

R_{int}	0.074
θ_{max} (°)	25.2
$\Delta\rho_{\mathrm{max}}$, $\Delta\rho_{\mathrm{min}}$ (e Å^{-3})	0.75, -1.15

Table S-2: Comparison of selected bond lengths (Å) in **L**$^{\mathbf{1}}$, **1** and **2.**

	L$^{\mathbf{1},\mathrm{v}}$	**1** $^{\mathrm{v}}$	**2**
Cu1-O1		2.084(5)	2.119(4)
Cu1-N1		2.001(8)	2.001(4)
Cu1-P1		2.261(2)	2.245(2)
Cu1-P2		2.245(3)	2.244(2)
Cu2-O2			2.100(3)
Cu2-N2			2.026(4)
Cu2-P3			2.255(2)
Cu2-P4			2.260(2)
C1-C2	1.398(2)	1.39(1)	1.397(7)
C1-C6	1.538(2)	1.50(1)	1.509(8)
C2-C3	1.401(2)	1.42(1)	1.383(7)
C3-C4	1.533(2)	1.50(1)	1.498(8)
C4-C5	1.393(2)	1.34(1)	1.416(7)
C5-C6	1.395(2)	1.43(1)	1.400(7)
C1-O1	1.251(2)	1.284(9)	1.262(6)
C6-N1	1.321(2)	1.30(1)	1.312(6)
C3-O2	1.252(2)	1.243(8)	1.287(6)
C4-N2	1.322(2)	1.35(1)	1.315(7)

Table S-3: Comparison of selected bond angles (°) in **1** and **2.**

	1	**2**
O1-Cu1-N1	78.9(3)	79.0(2)
O1-Cu1-P1	103.1(2)	109.5(1)
O1-Cu1-P2	119.0(2)	114.8(1)
N1-Cu1-P2	116.6(2)	120.3(2)
N1-Cu1-P1	122.3(2)	122.7(1)
P1-Cu1-P2	112.02(9)	107.2(5)
O2-Cu2-N2		80.0(2)
O2-Cu2-P4		108.0(1)
O2-Cu2-P3		113.1(1)
N2-Cu2-P3		114.4(1)
N2-Cu2-P4		126.0(1)
P3-Cu2-P4		110.7(5)

Table S-4. Redox potentials of ligand and complexes.[a]

Compound	$E_{1/2}$ (ox1)	$E_{1/2}$ (ox2)	E_{pc}[c] (red1)	E_{pc}[c] (red2)
L	0.91[b]	n.o.	-1.64	-2.24
1	0.32	0.70[b]	-1.99	n.o.[d]
2	-0.27	0.46	n.o.[d]	n.o.[d]

[a] Electrochemical potentials from cyclic voltammetry in CH_2Cl_2 / 0.1 M $[(n\text{-Bu})_4N]PF_6$. The couple Fc^0/Fc^+ was used as internal standard.
[b] Anodic peak potential for irreversible oxidation.
[c] Cathodic peak potential for irreversible reduction.
[d] n.o. = not observed.

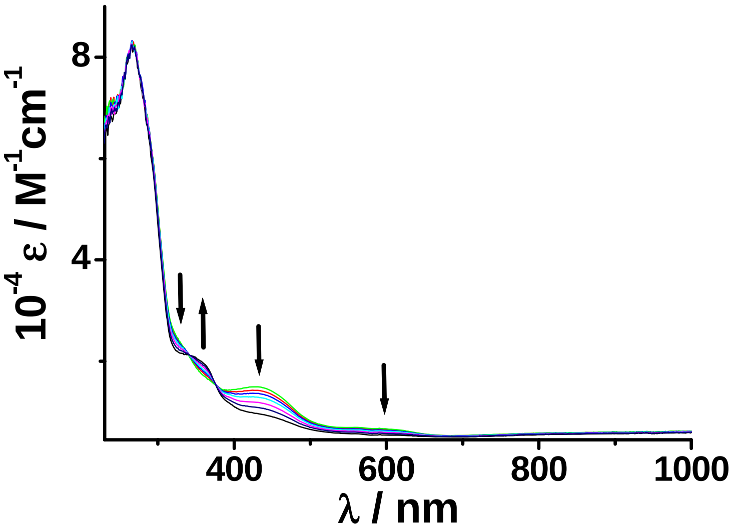

Figure S-1. Changes in the UV-vis spectrum of **2** during the first oxidation step in CH_2Cl_2/0.1 M [(*n*-Bu)$_4$N]PF_6 at 233 K.

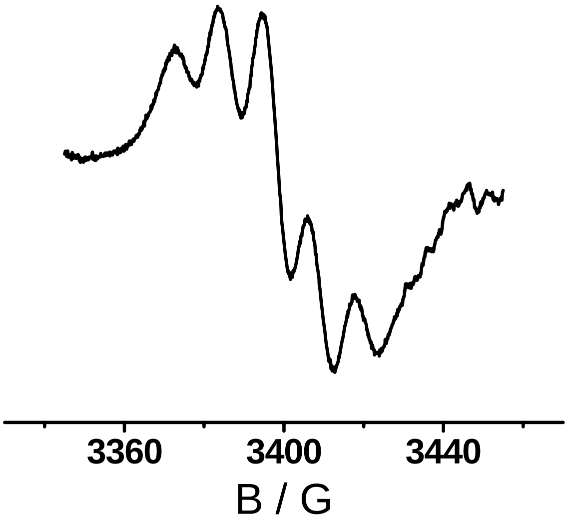

Figure S2. EPR spectrum of electrogenerated $\mathbf{2}^{\bullet+}$ in CH_2Cl_2 / 0.1 M [(*n*-Bu)$_4$N]PF_6 at 233 K.

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