ESI to accompany:

Phosphane tuning in heteroleptic [Cu(N^N)(P^P)]$^+$ complexes for light-emitting electrochemical cells

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Experimental details

General. Microwave reactions were performed in a Biotage Initiator 8 reactor. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance III-400, 500 and 600 NMR spectrometers; spectra were recorded at 295 K unless otherwise stated. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent peaks with respect to δ(TMS) = 0 ppm and ^{31}P NMR chemical shifts with respect to δ(85% aqueous H_3PO_4) = 0 ppm.

Solid-state IR spectra were recorded using Perkin Elmer UATR Two spectrometer. Solution absorption and emission spectra were measured using an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC spectrofluorometer, respectively. A Shimadzu LCMS-2020 instrument or a Bruker esquire 3000plus instrument was used to record electrospray ionization (ESI) mass spectra. Quantum yields (CH_2Cl_2 solution and powder) were measured using a Hamamatsu absolute

photoluminescence quantum yield spectrometer C11347 Quantaurus-QY. Emission lifetimes and powder emission spectra were measured with a Hamamatsu Compact Fluorescence lifetime Spectrometer C11367 Quantaurus-Tau, using an LED light source with λ_{exc} = 280 or 365 nm (see text). Quantum yields and PL emission spectra in thin films were recorded using a Hamamatsu absolute quantum yield C9920. Low temperature emission and lifetime experiments were performed using an LP920-KS instrument from Edinburgh Instruments. 410 nm excitation was obtained from pulsed third-harmonic radiation from a Quantel Brilliant b Nd:YAG laser equipped with a Rainbow optical parameter oscillator (OPO). The laser pulse duration was ~10 ns and the pulse frequency 10 Hz, with a typical pulse energy of 7 mJ. Detection of the spectra occurred on an iCCD camera from Andor. Single-wavelength kinetics were recorded using a photomultiplier tube. Electrochemical measurements were carried out using a CH Instruments 900B potentiostat with [^{n}Bu$_4$N][PF$_6$] (0.1 M) as supporting electrolyte and at a scan rate of 0.1 V s^{-1}. The working electrode was glassy carbon, the reference electrode was a leakless Ag$^+$/AgCl (eDAQ ET069-1) and the counter-electrode was a platinum wire. Final potentials were internally referenced with respect to the Fc/Fc$^+$ couple.

6-Methyl-2,2'-bipyridine (6-Mebpy). The compound was prepared by an adapted literature method.[1] A microwave flask was charged with [Pd(PPh$_3$)$_4$] (342 mg, 0.296 mmol), then evacuated and backfilled with N_2 three times. 2-Pyridylzinc bromide in a solution of THF (0.5 M, 18.0 mL, 9.0 mmol) and 2-chloro-6-methylpyridine (0.70 mL, 6.44 mmol) were added and the mixture was degassed with N_2 for 20 min. The reaction was performed in a microwave reactor at 110 °C for 2 h. A saturated solution of NaHCO$_3$ (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 40 mL).

The combined organic layers were washed with water (3 x 30 mL) and dried over $MgSO_4$. The solvent was removed and the crude material was purified by flash chromatography (Alox, cyclohexane : ethyl acetate 20 : 1) to give 6-Mebpy as a pale yellow oil. The NMR spectroscopic data were in agreement with the literature. ESI MS: *m/z* 171.0 $[M + H]^+$ (base peak, calc. 171.1).

xantphosMes$_4$. The compound was prepared by adapting a literature procedure.[2] 9,9-Dimethylxanthene (265 mg, 1.26 mmol) was dissolved in dry heptane (30 mL) under inert conditions. A solution of ^{n}BuLi (1.6 M in hexane, 1.97 mL, 3.15 mmol) and tetramethylethylenediamine (475 µL, 3.15 mmol) were added and the mixture was stirred at reflux for 30 min. The mixture was cooled to room temperature and added slowly to a solution of Mes_2PCl (1.00 g, 3.28 mmol) in THF (10 mL) at 0 °C. After stirring for 1 h at 0 °C, the reaction mixture was allowed to warm up over 50 h, diluted with ethyl acetate (20 mL) and washed with water (30 mL). The aqueous phase was extracted with ethyl acetate (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$ and the solvent was removed. The resulting crude oil was sonicated with ethyl acetate (2 mL) until white crystals precipitated. Crystalline xantphosMes$_4$ was collected by filtration (232 mg, 0.31 mmol, 24.7 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ/ppm: 7.38 (d, J = 7.7 Hz, 2H, H^{C5}), 6.87 (t, J = 7.6 Hz, 2H, H^{C4}), 6.75–6.67 (overlapping m, 10H, H^{C3+E3}), 2.21 (s, 12H, H^{MeE4}), 1.89 (s, 24H, H^{MeE2}), 1.67 (s, 6H, H^{MeCq1}). ^{13}C NMR (126 MHz, CD_2Cl_2) δ/ppm: 153.4 (C^{C1}), 143.3 (t, J_{PC} = 8.5 Hz, C^{E1}), 137.7 (C^{E4}), 131.88 (C^{C3}), 131.87 (C^{E2}), 130.1 (C^{E3}), 129.9 (C^{C6}), 126.7 (C^{C5}), 123.4 (C^{C4}), 34.7 (C^{Cq1}), 33.0 (C^{MeE4}), 22.7 (t, J_{PC} = 8.3 Hz, C^{MeE2}), 21.2 (C^{MeCq1}), C2 not resolved. ^{31}P NMR (202 MHz, CD_2Cl_2) δ/ppm: –36.2. ESI-MS: *m/z* 747.3 $[M+H]^+$ (base peak, calc. 747.4).

Chloro(mesityl)phenylphosphane. Bromomesitylene (3.38 g, 17.0 mmol) was dissolved in dry THF (10 mL) under inert conditions. Part of this solution (2 mL) was added to a round bottomed flask with Mg turnings (455 mg, 18.7 mmol) and heated to reflux. To initiate the reaction, a small amount of *t*-BuMgCl (1 M solution in THF) and iodine were added and after the reaction had started, the rest of the bromomesitylene solution was added slowly. The mixture was stirred at reflux for 3 h. After cooling to room temperature the mixture was added dropwise over 1 h to a solution of $PhPCl_2$ (2.30 mL, 17.0 mmol) at –78 °C. After warming to room temperature, the mixture was stirred for 2 h. The solvent was removed under Schlenk conditions and the crude material was used in the next step without further purification.

xantphosMes_2. The compound was prepared by adapting a literature procedure.[2] 9,9-Dimethylxanthene (1.32 g, 6.30 mmol) was dissolved in dry heptane (30 mL) under inert conditions. A solution of ^{n}BuLi (1.6 M in hexane, 9.84 mL, 15.8 mmol) and tetramethylethylenediamine (2.38 mL, 15.8 mmol) were added and the mixture was stirred at reflux for 20 min. The mixture was cooled to room temperature and added slowly to a solution of crude chloro(mesityl)phenylphosphane in THF (10 mL) at 0 °C. After stirring for 1 h at 0 °C, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (30 mL). The aqueous phase was extracted with ethyl acetate (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$ and the solvent was removed. The crude material was purified by column chromatography (silica, ethyl acetate : cyclohexane 1:2 + 1% triethylamine). The resulting material was dissolved in a little ethyl acetate and precipitated and washed with EtOH to give xantphosMes_2 (874 mg, ≈1.32 mmol, ≈21 %, analytically pure xantphosMes_2 could not

be obtained) as a white powder. ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 7.59 (d, J = 7.8 Hz, 2H, H^{C5}), 7.19–7.15 (overlapping m, 6H, H^{D3+D4}), 7.08 (m, 4H, H^{D2}), 7.02 (t, J = 7.6 Hz, 2H, H^{C4}), 6.78 (s, 4H, H^{E3}), 6.67 (m, 2H, H^{C3}), 2.21 (s, 6H, H^{MeE4}), 1.94 (s, 12H, H^{MeE2}), 1.78 (s, 6H, H^{MeCq1}). ^{13}C NMR (126 MHz, acetone-d_6) δ/ppm: 152.8 (t, 9.6 Hz, C^{C1}), 145.9 (t, 8.7 Hz, C^{E2}), 140.1 (C^{E4}), 132.6 (t, 10.5 Hz, C^{D2}), 131.2 (C^{C3}), 130.7 (C^{C6}), 130.6 (t, 2.0 Hz, C^{E3}), 130.1 (C^{E1}), 128.4 (t, 3.3 Hz, C^{D3}), 127.49 (C^{D4}), 127.46 (C^{C5}), 124.4 (C^{C4}), 124.3 (C^{C2}), 35.2 (C^{Cq1}), 32.9 (C^{MeCq1}), 23.9 (C^{MeE2}), 21.1 (C^{MeE4}), C^{D1} not resolved. ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –25.8. ESI-MS: *m/z* 663.5 $[M+H]^+$ (base peak, calc. 663.3). Satisfactory elemental analysis could not be obtained.

[Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$]. $[Cu(MeCN)_4][PF_6]$ (93.2 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (15 mL). A solution of ^{t}Bu$_2$xantphos (174 mg, 0.25 mmol) and bpy (39.0 mg, 0.25 mmol) was added and the mixture was stirred for 1 h at room temperature during which time it turned orange. This colour indicated the presence of homoleptic $[Cu(bpy)_2][PF_6]$ and therefore additional *t*-Bu-xantphos (33.0 mg, 0.05 mmol) was added. The solution was stirred for another 2.5 h during which time it turned yellow. The solution was filtered and the solvent was removed from the filtrate under reduced pressure. The solid product was washed with Et_2O (3 × 40 mL) and dried under vacuum. $[Cu(^tBu_2xantphos)(bpy)][PF_6]$ (226 mg, 0.21 mmol, 85.6%) was isolated as a yellow solid. ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 8.61 (dt, J = 8.2, 1.0 Hz, 1H, H^{A3}), 8.24 (ddd, J = 5.1, 1.6, 0.8 Hz, 1H, H^{A6}), 8.16 (td, J = 7.8, 1.7 Hz, 1H, H^{A4}), 7.86 (d, J = 2.2 Hz, 2H, H^{C5}), 7.44 (ddd, J = 7.6, 5.1, 1.1 Hz, 1H, H^{A5}), 7.35 (m, 4H, H^{D4}), 7.22 (m, 8H, H^{D3}), 7.02 (m, 8H, H^{D2}), 6.59 (m, 2H, H^{C3}), 1.82 (s, 6H, H^{MeCq1}), 1.11 (s, 18 H, $H^{t\text{-}Bu}$). ^{13}C NMR (126 MHz, acetone-d_6) δ/ppm: 154.2 (C^{C1}), 152.8 (C^{A2}), 150.1 (C^{A6}), 148.5 (C^{C4}), 139.9 (C^{A4}), 133.7 (t, 8.0 Hz, C^{D2}), 132.8 (C^{C6}), 132.6 (C^{D1}), 130.9 (C^{D4}), 129.7 (t,

4.7 Hz, C^{D3}), 128.6 (C^{C3}), 127.1 (C^{A5}), 125.2 (C^{C5}), 123.8 (C^{A3}), 119.7 (C^{C2}), 37.6 (C^{Cq1}), 35.5 (C^{Cq2}), 31.5 ($C^{t\text{-}Bu}$), 28.2 (C^{MeCq1}). ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –11.3 (broad, FWHM = 230 Hz), –144.3 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). ESI MS: *m/z* 909.2 $[M–PF_6]^+$ (base peak, calc. 909.3). UV-Vis (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 229 (44300), 244sh (34300), 283 (30000), 385 (3200). Found: C 64.47, H 6.17, N 2.38; $C_{57}H_{56}CuF_6N_2OP_3$ requires C 64.86, H 5.35, N 2.65%. See Fig. S6 for IR spectrum.

[Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF$_6$]. [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF_6] was prepared using the procedure described for [Cu(^{t}Bu$_2$xantphos)(bpy)][PF_6] starting with $[Cu(MeCN)_4][PF_6]$ (93.2 mg, 0.25 mmol), ^{t}Bu$_2$xantphos (207 mg, 0.30 mmol) and 6-Mebpy (42.6 mg, 0.25 mmol). [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF_6] was isolated as a yellow powder (226 mg, 0.21 mmol, 84.5%). ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 8.51 (dt, *J* = 8.3, 1.0 Hz, 1H, H^{A3}), 8.44–8.41 (overlapping m, 2H, H^{A6+B3}), 8.12 (t, *J* = 7.9 Hz, 1H, H^{B4}), 8.09 (m, 1H, H^{A4}), 7.84 (d, *J* = 2.2 Hz, 2H, H^{C5}), 7.49 (d, *J* = 7.7 Hz, 1H, H^{B5}), 7.46 (ddd, *J* = 7.6, 5.1, 1.1 Hz, 1H, H^{A5}), 7.40 (m, 2H, H^{D4}), 7.35 (m, 2H, $H^{D4'}$), 7.27 (m, 4H, H^{D3}), 7.23–7.16 (overlapping m, 8H, $H^{D2+D3'}$), 6.96 (m, 4H, $H^{D2'}$), 6.65 (m, 2H, H^{C3}), 2.01 (s, 3H, H^{MeB6}), 1.91 (s, 3H, H^{MeCq1}), 1.71 (s, 3H, $H^{MeCq1'}$), 1.12 (s, 18H, $H^{t\text{-}Bu}$). ^{13}C NMR (126 MHz, acetone-d_6) δ/ppm: 159.4 (C^{B6}), 154.3 (C^{C1}), 153.4 (C^{A2}), 152.5 (C^{B2}), 149.9 (C^{A6}), 148.8 (C^{C4}), 140.2 (C^{B4}), 139.8 (C^{A4}), 134.7 (C^{C6}), 133.8 (t, 7.9 Hz, $C^{D2'}$), 133.6 (t, 7.9 Hz, C^{D2}), 131.0 ($C^{D4'}$), 130.9 (C^{D4}), 129.8 (t, 4.4 Hz, C^{D3}), 129.6 (t, 4.4 Hz, $C^{D3'}$), 128.2 (C^{C3}), 126.89 (C^{B5}), 126.86 (C^{A5}), 125.2 (C^{C5}), 123.8 (C^{A3}), 121.0 (C^{B3}), 37.5 (C^{Cq1}), 35.5 (C^{Cq2}), 31.5 ($C^{t\text{-}Bu}$), 29.1 ($C^{MeCq'}$), 26.4 (C^{MeCq1}), 26.0 (C^{MeB6}), C^{C2} not resolved. ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –11.6 (broad, FWHM = 250 Hz), –144.3 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). ESI MS: *m/z* 923.2 $[M–PF_6]^+$ (base peak, calc. 923.3). HR ESI MS: *m/z* 923.3327 $[M–PF_6]^+$ (calc. 923.3315). UV-Vis (CH_2Cl_2, 2.5 × 10^{-5}

mol dm^{-3}): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 228 (45900), 244sh (34700), 284 (30000), 311sh (13600), 383 (3400). Found: C 64.95, H 6.44, N 2.70; $C_{58}H_{58}CuF_6N_2OP_3$ requires C 65.13, H 5.47, N 2.62%. See Fig. S7 for IR spectrum.

[Cu(^{t}Bu$_2$xantphos)(6,6'-Me$_2$bpy)][PF$_6$]. [Cu(^{t}Bu$_2$xantphos)(6,6'-Me$_2$bpy)][PF$_6$] was prepared according to the procedure described for [Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$] using [Cu(MeCN)$_4$][PF$_6$] (93.2 mg, 0.25 mmol), ^{t}Bu$_2$xantphos (207 mg, 0.30 mmol) and 6,6'-Mebpy (46.1 mg, 0.25 mmol). [Cu(^{t}Bu$_2$xantphos)(6,6'-Me$_2$bpy)][PF$_6$] was isolated as a yellow powder (118 mg, 0.11 mmol, 43.6%). ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 8.16 (d, J = 8.0 Hz, 2H, H^{B3}), 7.97 (t, J = 7.8 Hz, 2H, H^{B4}), 7.82 (d, J = 2.2 Hz, 2H, H^{C5}), 7.41 (m, 4H, H^{D4}), 7.37 (d, J = 7.4 Hz, 2H, H^{B5}), 7.25 (m, 8H, H^{D3}), 7.20 (m, 8H, H^{D2}), 6.95 (m, 2H, H^{C3}), 2.09 (s, 6H, H^{MeB6}), 1.79 (s, 6H, H^{MeCq1}), 1.16 (s, 18H, H$^{t\text{-}Bu}$). ^{13}C NMR (126 MHz, acetone-d$_6$) δ/ppm: 159.3 (C^{B6}), 154.2 (C^{C1}), 153.1 (C^{B2}), 148.8 (C^{C4}), 139.8 (C^{B4}), 134.6 (C^{C6}), 134.0 (t, 7.7 Hz, C^{D2}), 132.7 (C^{D1}), 130.9 (C^{D4}), 129.6 (t, 4.4 Hz, C^{D3}), 127.9 (C^{C3}), 126.3 (C^{B5}), 125.3 (C^{C5}), 121.0 (C^{B3}), 37.5 (C^{Cq1}), 35.6 (C^{Cq2}), 31.5 (C$^{t\text{-}Bu}$), 28.5 (C^{MeCq1}), 26.8 (C^{MeB6}), C^{C2} not resolved. ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –12.6 (broad, FWHM = 280 Hz), –144.3 (septet, J_{PF} = 707 Hz, [PF$_6$]$^-$). ESI MS: *m/z* 937.2 [M–PF$_6$]$^+$ (base peak, calc. 923.4). UV-Vis (CH$_2$Cl$_2$, 2.5 × 10^{-5} mol dm^{-3}): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 229 (46700), 244sh (34500), 283 (27000), 317sh (12100), 377 (2700). Found: C 64.88, H 5.78, N 2.41; $C_{59}H_{60}CuF_6N_2OP_3$ requires C 65.40, H 5.58, N 2.59%. See Fig. S8 for IR spectrum.

[Cu(xantphosMes$_2$)(bpy)][PF$_6$]. [Cu(xantphosMes$_2$)(bpy)][PF$_6$] was prepared using the procedure described for [Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$] starting with [Cu(MeCN)$_4$][PF$_6$] (93.2 mg, 0.25 mmol), xantphosMes$_2$ (199 mg, 0.30 mmol) and bpy (39.0 mg, 0.25 mmol). [Cu(xantphosMes$_2$)(bpy)][PF$_6$] was isolated as a yellow powder (224 mg, 0.22

mmol, 87.2%). ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 8.70 (dt, J = 8.3, 1.0 Hz, 2H, H^{A3}), 8.17 (td, J = 7.8, 1.7 Hz, 2H, H^{A4}), 7.95 (d, J = 4.9 Hz, 2H, H^{A6}), 7.89 (dd, J = 7.8, 1.4 Hz, 2H, H^{C5}), 7.36 (ddd, J = 7.8, 5.2, 1.1 Hz, 2H, H^{A5}), 7.21 (t, J = 7.7 Hz, 2H, H^{C4}), 7.16 (t, J = 7.4 Hz, 2H, H^{D4}), 7.01 (m, 4H, H^{D3}), 6.91 (m, 4H, H^{D2}), 6.71 (s, 4H, H^{E3}), 6.49 (m, 2H, H^{C3}), 2.24 (s, 6H, H^{MeE4}), 1.92 (s, 6H, H^{MeCq1}), 1.82 (s, 12H, H^{MeE2}). ^{13}C NMR (126 MHz, acetone-d_6) δ/ppm: 156.0 (t, 6.2 Hz, C^{C1}), 152.8 (C^{A2}), 149.8 (C^{A6}), 144.0 (t, 5.7 Hz, C^{E2}), 140.9 (C^{E4}), 140.1 (C^{A4}), 134.7 (C^{C6}), 133.8 (t, 16.7 Hz, C^{D1}), 132.1 (t, 7.4 Hz, C^{D2}), 131.93 (C^{E3}), 131.88 (C^{C3}), 129.8 (C^{D4}), 129.3 (t, 4.4 Hz, C^{D3}), 128.3 (C^{C5}), 126.9 (C^{A5}), 126.3 (t, 2.3 Hz, C^{C4}), 124.8 (t, 14.1 Hz, C^{E1}), 124.1 (C^{A3}), 121.4 (t, 11.5 Hz, C^{C2}), 36.8 (C^{Cq1}), 28.3 (C^{MeCq1}), 23.7 (C^{MeE2}), 20.9 (C^{MeE4}). ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –21.7 (broad, FWHM = 360 Hz), –144.3 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). ESI MS: m/z 725.4 $[Cu(xantphosMes_2)]^+$ (base peak, calc. 725.2), 881.5 $[M–PF_6]^+$ (calc. 881.3). UV-Vis (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 230 (50000), 240sh (44000), 285 (30000), 386 (2900). Found: C 63.53, H 5.56, N 2.95; $C_{55}H_{52}CuF_6N_2OP_3$ requires C 64.29, H 5.10, N 2.73%. See Fig. S9 for IR spectrum.

[Cu(xantphosMes$_2$)(6-Mebpy)][PF$_6$]. [Cu(xantphosMes$_2$)(6-Mebpy)][PF$_6$] was prepared by the same procedure as for [Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$] starting with [Cu(MeCN)$_4$][PF$_6$] (93.2 mg, 0.25 mmol), xantphosMes$_2$ (199 mg, 0.30 mmol) and 6-Mebpy (42.6 mg, 0.25 mmol). [Cu(xantphosMes$_2$)(6-Mebpy)][PF$_6$] was isolated as a yellow powder (241 mg, 0.23 mmol, 92.6%). ^{1}H NMR (500 MHz, acetone-d_6) δ/ppm: 8.63 (ddd, J = 5.2, 1.6, 0.9 Hz, 1H, H^{A6}), 8.59 (d, J = 8.2 Hz, 1H, H^{A3}), 8.55 (d, J = 7.9 Hz, 1H, H^{B3}), 8.18–8.12 (overlapping m, 2H, H^{A4+B4}), 7.85 (m, 2H, $H^{C5+C5'}$), 7.51 (ddd, J = 7.6, 5.2, 1.1 Hz, 1H, H^{A5}), 7.44 (d, J = 7.7 Hz, 1H, H^{B5}), 7.29–7.18 (overlapping m, 5H, $H^{C4+C4'+D4+D2'}$), 7.14 (m, 1H, $H^{D4'}$), 7.04 (m, 4H, $H^{D3+D3'}$), 6.74 (s, 2H, H^{E3}), 6.72–6.66 (overlapping m, 3H, $H^{E3'+C3}$), 6.62 (m, 2H, H^{D2}), 6.48 (m, 1H, $H^{C3'}$), 2.27 (s,

3H, $H^{MeE4'}$), 2.22 (s, 3H, H^{MeE4}), 1.94 (s, 3H, H^{MeCq1}), 1.83 (s, 6H, $H^{MeE2'}$), 1.76 (s, 3H, H^{MeB6}), 1.75 (s, 3H, $H^{MeCq1'}$), 1.69 (s, 6H, H^{MeE2}). ^{13}C NMR (126 MHz, acetone-d_6) δ/ppm: 159.9 (C^{B6}), 156.4 (C^{C1}), 155.4 ($C^{C1'}$), 153.6 (C^{A2}), 152.9 (C^{B2}), 150.6 (C^{A6}), 144.7 (C^{E2}), 143.2 ($C^{E2'}$), 141.2 (C^{E4}), 140.4 (C^{B4}), 140.3 ($C^{E4'}$), 140.2 (C^{A4}), 134.9 (C^{D1}), 134.5 (C^{C6}), 134.1 ($C^{C6'}$), 132.9 (C^{D2}), 133.7 ($C^{D1'}$), 132.3 ($C^{C3'}$), 132.0 ($C^{E3'}$), 131.95 ($C^{D2'}$), 131.90 (C^{C3}), 131.8 (C^{E3}), 130.5 (C^{D4}), 129.6 (m, $C^{D3+D3'+D4'}$), 128.5 ($C^{C5+C5'}$), 127.2 (C^{B5}), 126.8 (C^{A5}), 126.3 (C^{C4}), 126.1 ($C^{C4'}$), 125.3 (C^{E1}), 124.8 ($C^{E1'}$), 123.87 (C^{A3}), 121.3 (C^{B3}), 36.6 (C^{Cq1}), 30.9 (broadened, $C^{MeCq1'}$), 26.6 (broadened, C^{MeCq1}), 25.6 (C^{MeB6}), 23.9 ($C^{MeE2'}$), 23.5 (C^{MeE2}), 20.8 ($C^{MeE4+MeE4'}$), C^{C2} not resolved. ^{31}P NMR (202 MHz, acetone-d_6) δ/ppm: –21.2 (broad, FWHM = 280 Hz), –144.3 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). ESI MS: *m/z* 725.4 $[Cu(xantphosMes_2)]^+$ (base peak, calc. 725.2), $[M–PF_6]^+$ not observed. UV-Vis (CH_2Cl_2, 2.5 × 10^{-5} mol dm^{-3}): λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 230 (53000), 240sh (45000), 287 (32000), 381 (2800). Found: C 64.54, H 5.89, N 2.90; $C_{56}H_{54}CuF_6N_2OP_3$ requires C 64.58, H 5.23, N 2.69%. See Fig. S10 for IR spectrum.

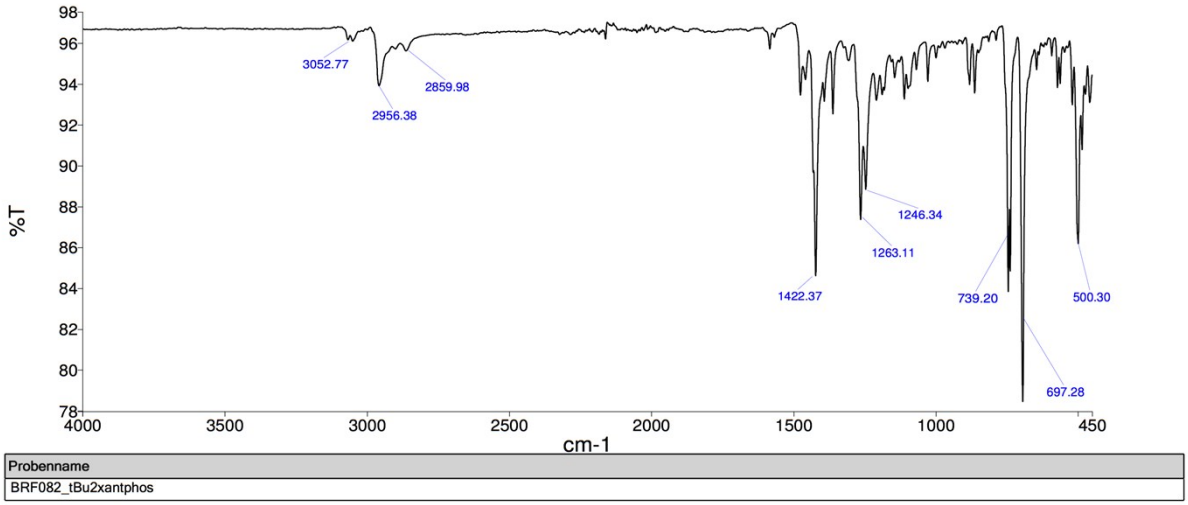


Fig. S1. IR spectrum of tBu_2xantphos (solid state).

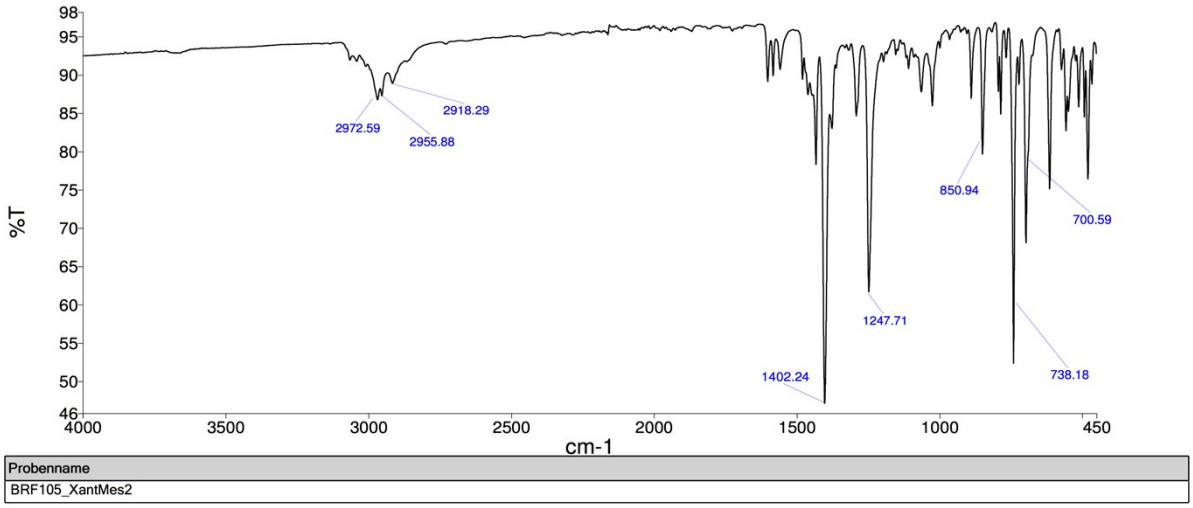


Fig. S2. IR spectrum of xantphosMe$_2$ (solid state).

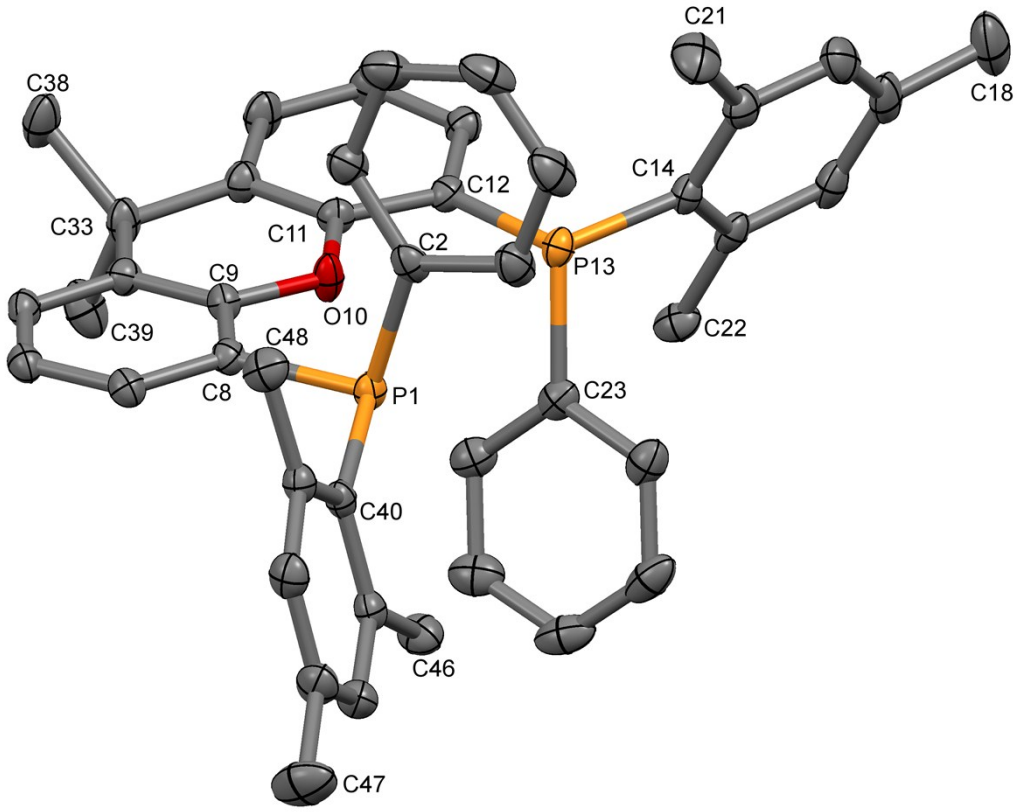


Fig. S3. Molecular structure of xantphosMes$_2$ with ellipsoids plotted at 50% probability level; H atoms are omitted for clarity. Selected bond parameters: P1–C2 = 1.8326(14), P1–C8 = 1.8432(13), P1–C40 = 1.8492(14), P13–C12 = 1.8357(13), P13–C14 = 1.8417(14), P13–C23 = 1.8378(15), C9–O10 = 1.3758(16), O10–C11 = 1.3746(16) Å; C2–P1–C8 = 103.30(6), C2–P1–C40 = 106.26(6), C8–P1–C40 = 102.94(6), C12–P13–C14 = 102.10(6), C12–P13–C23 = 103.57(6), C14–P13–C23 = 104.92(6), C9–O10–C11 = 120.07(10)°.

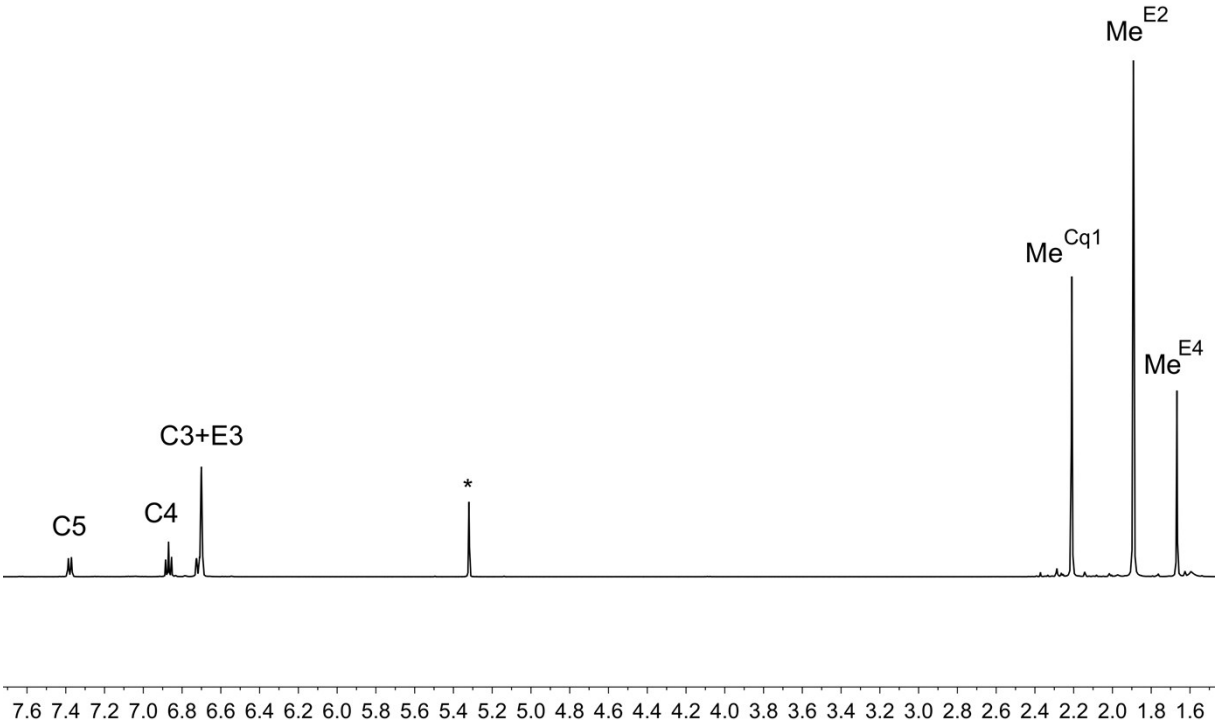


Fig. S4. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of xantphosMe_4, assigned by 2D methods. See Scheme 3 for atom labels. * = residual $CDHCl_2$.

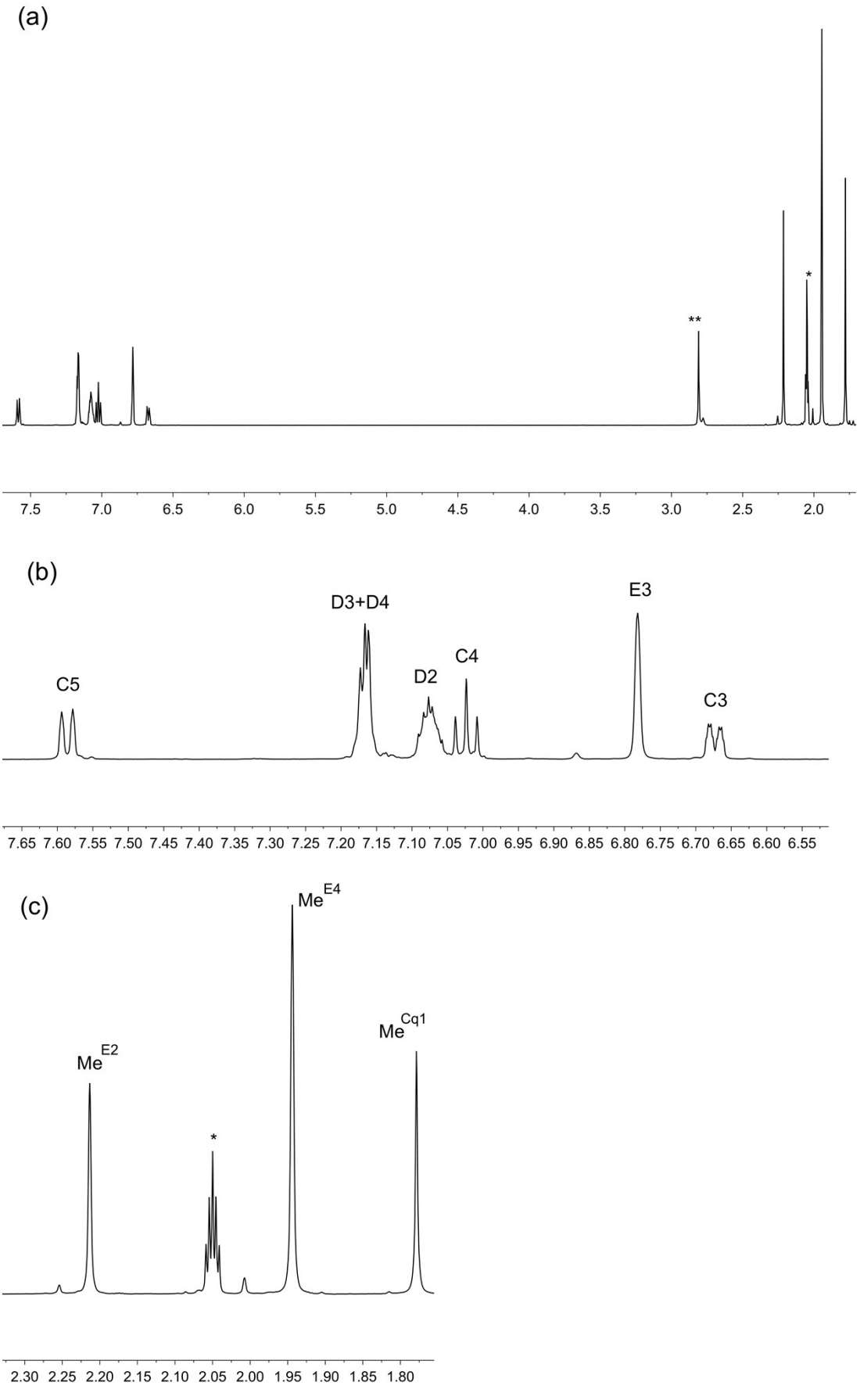
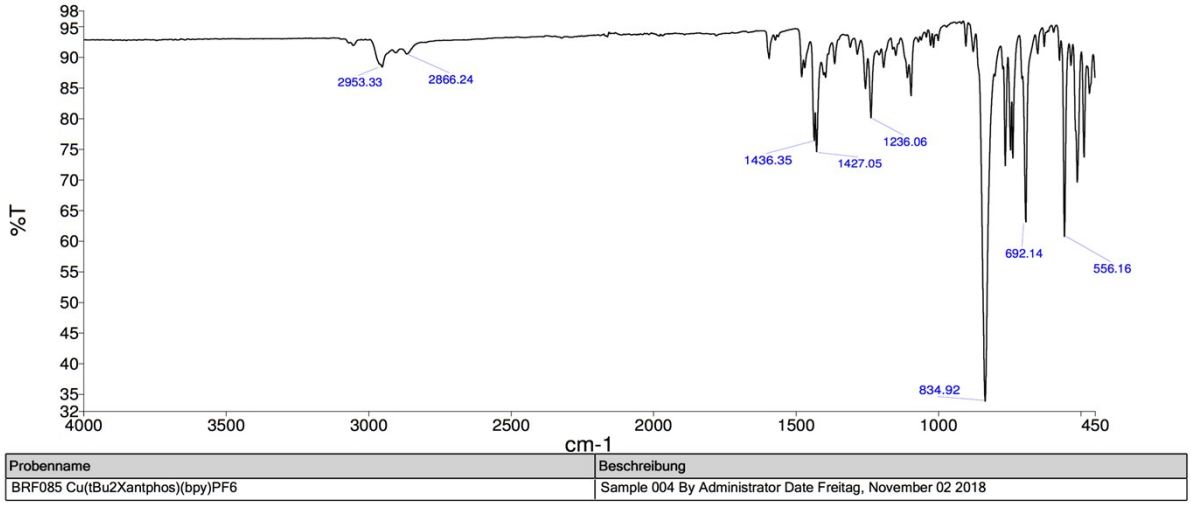
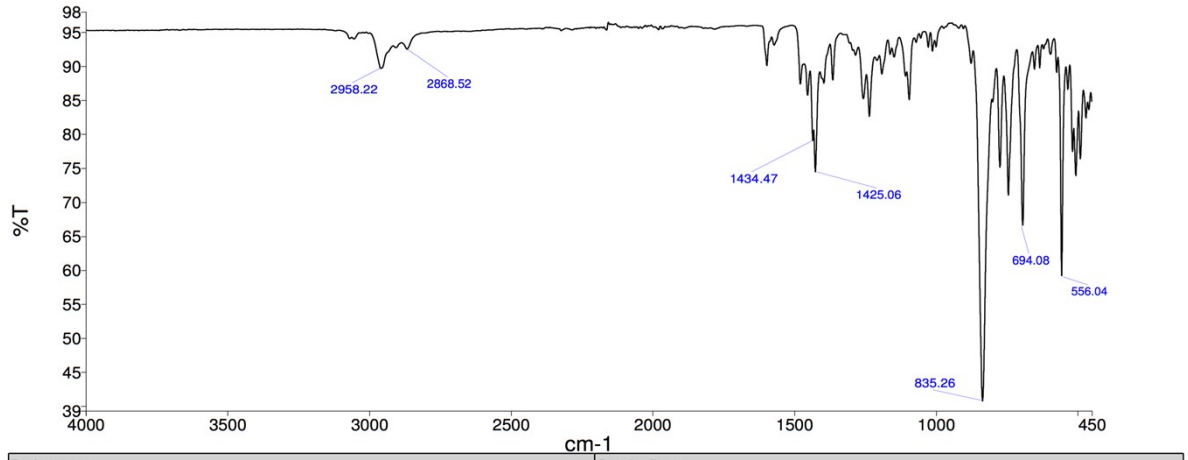


Fig. S5. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of xantphosMes$_2$, assigned by 2D methods. See Scheme 3 for atom labels. * = residual acetone-d_5, ** = water. (a) Full spectrum, (b) expansion of aromatic region, (c) expansion of aliphatic region.



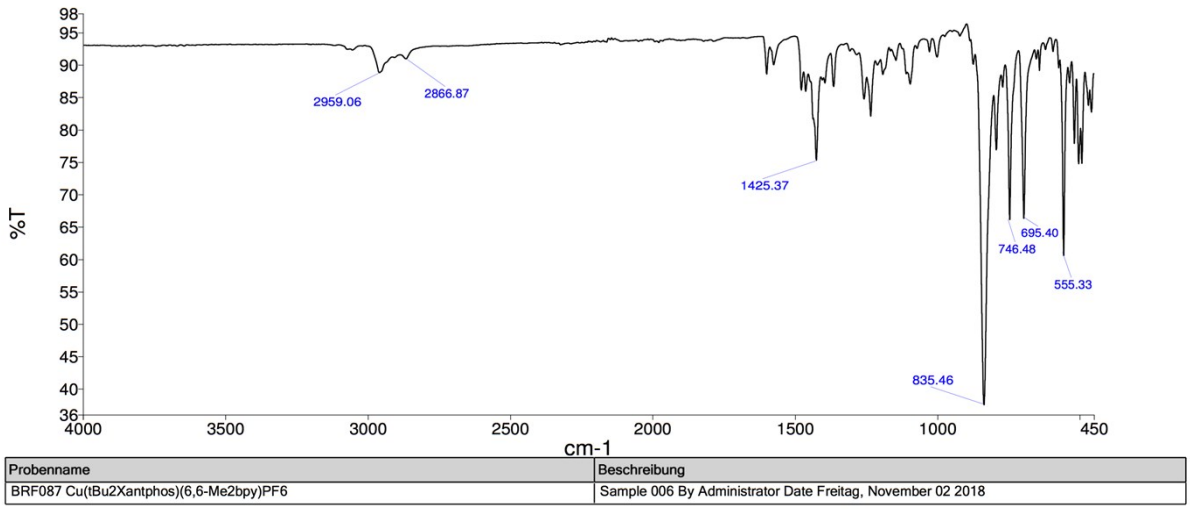
Probenname	Beschreibung
BRF085 Cu(tBu2Xantphos)(bpy)PF6	Sample 004 By Administrator Date Freitag, November 02 2018

Fig. S6. IR spectrum of [Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$] (solid state).



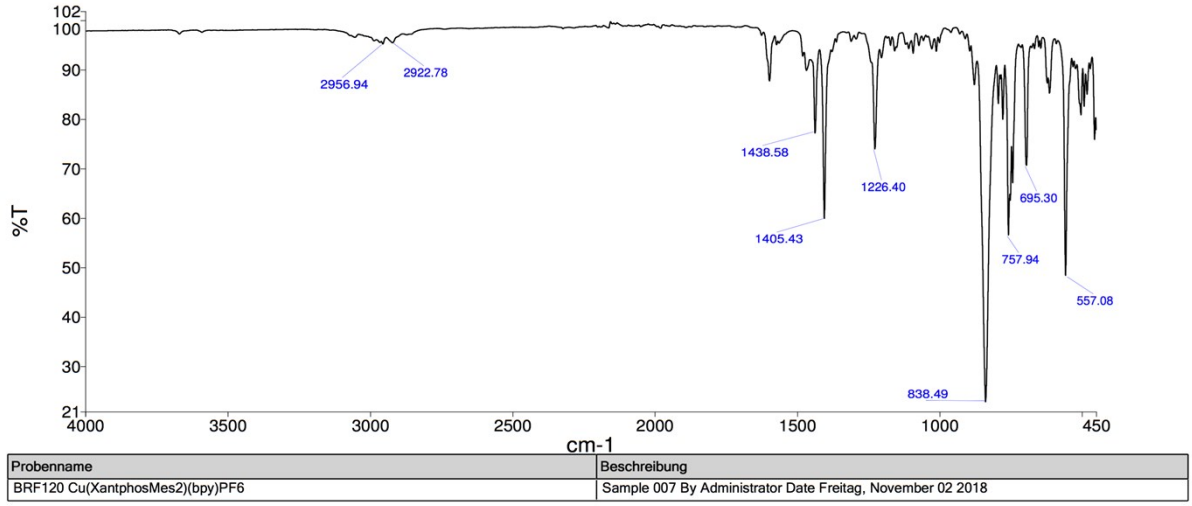
Probenname	Beschreibung
BRF086 Cu(tBu2Xantphos)(6-Mebpy)PF6	Sample 005 By Administrator Date Freitag, November 02 2018

Fig. S7. IR spectrum of [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF$_6$] (solid state).



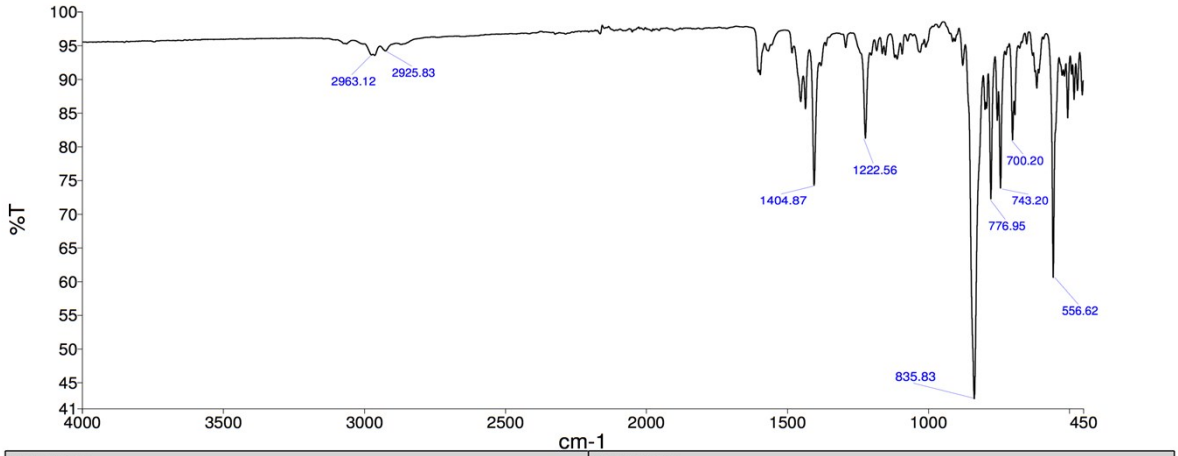
Probenname	Beschreibung
BRF087 Cu(tBu2Xantphos)(6,6-Me2bpy)PF6	Sample 006 By Administrator Date Freitag, November 02 2018

Fig. S8. IR spectrum of [Cu(^{t}Bu$_2$xantphos)(6,6'-Me$_2$bpy)][PF$_6$] (solid state).



Probenname	Beschreibung
BRF120 Cu(XantphosMes2)(bpy)PF6	Sample 007 By Administrator Date Freitag, November 02 2018

Fig. S9. IR spectrum of [Cu(xantphosMes$_2$)(bpy)][PF$_6$] (solid state).



Probenname	Beschreibung
BRF121 Cu(XantphosMes2)(6-Mebpy)PF6	Sample 008 By Administrator Date Freitag, November 02 2018

Fig. S10. IR spectrum of [Cu(xantphosMes$_2$)(6-Mebpy)][PF$_6$] (solid state).

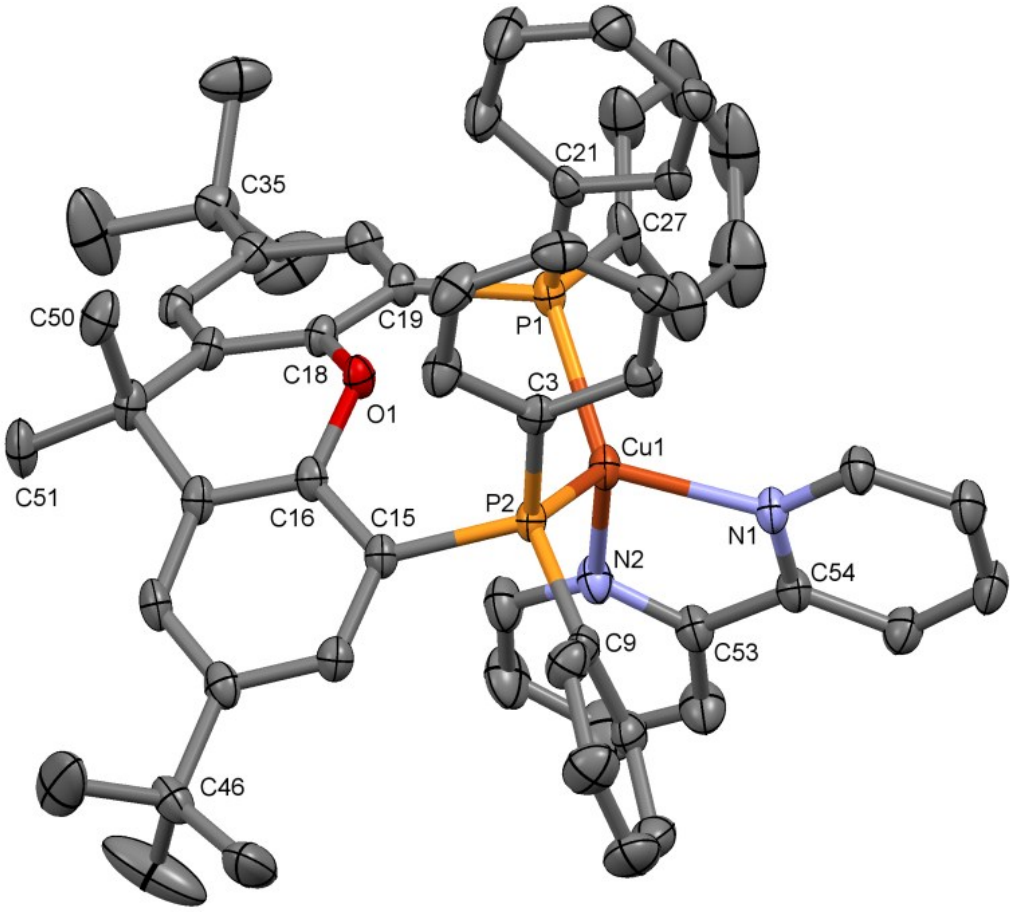


Fig. S11. Structure of the $[Cu(^tBu_2xantphos)(bpy)]^+$ cation in $[Cu(^tBu_2xantphos)(bpy)][PF_6]\cdot 0.5Et_2O$ with ellipsoids plotted at 50% probability level; H atoms are omitted for clarity. Selected bond parameters: Cu1–P1 = 2.2580(6), Cu1–P2 = 2.2522(6), Cu1–N1 = 2.056(2), Cu1–N2 = 2.070(2) Å; P1–Cu1–P2 = 113.56(2), P1–Cu1–N1 = 118.71(5), P2–Cu1–N1 = 112.59(5), P1–Cu1–N2 = 110.19(5), P2–Cu1–N2 = 117.97(5), N1–Cu1–N2 = 79.90(7)°.

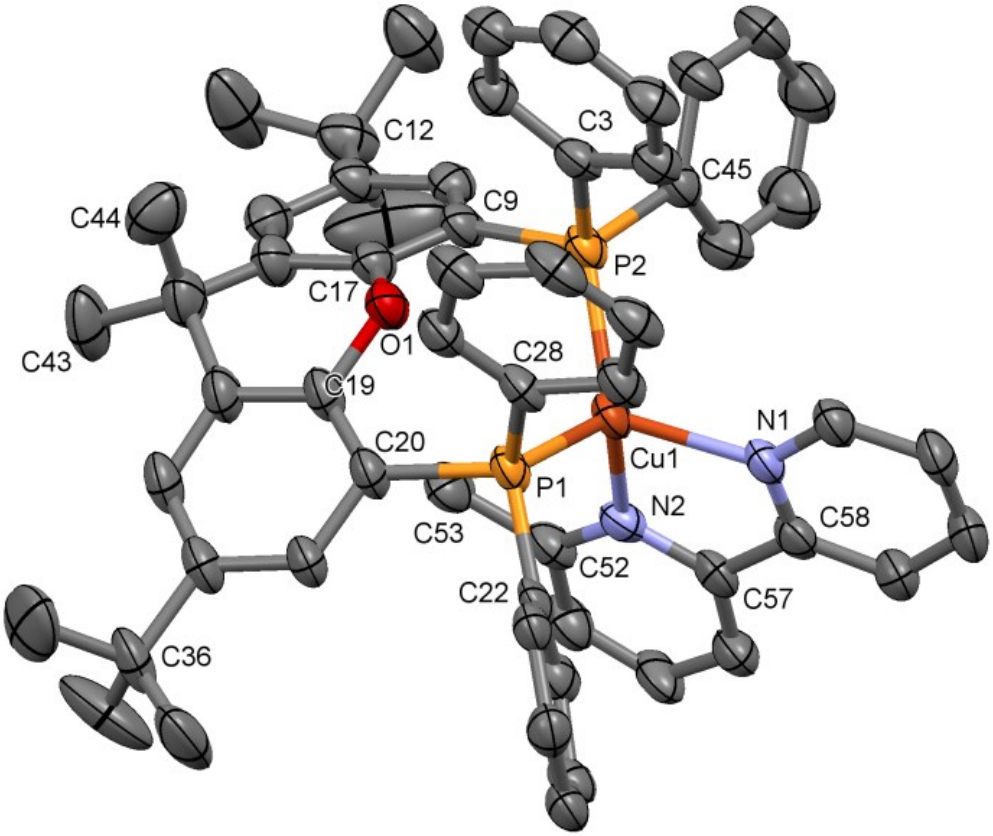


Fig. S12. Structure of the [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)]$^+$ cation in [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF$_6$]·1.5CH$_2$Cl$_2$·0.5H$_2$O with ellipsoids plotted at 50% probability level; H atoms are omitted for clarity. Selected bond parameters: Cu1–P1 = 2.277(2), Cu1–P2 = 2.254(2), Cu1–N1 = 2.065(6), Cu1–N2 = 2.081(4) Å; P1–Cu1–P2 = 112.70(7), P1–Cu1–N1 = 112.1(2), P2–Cu1–N1 = 115.9(2), P1–Cu1–N2 = 114.9(1), P2–Cu1–N2 = 117.3(1), N1–Cu1–N2 = 80.1(2)°.

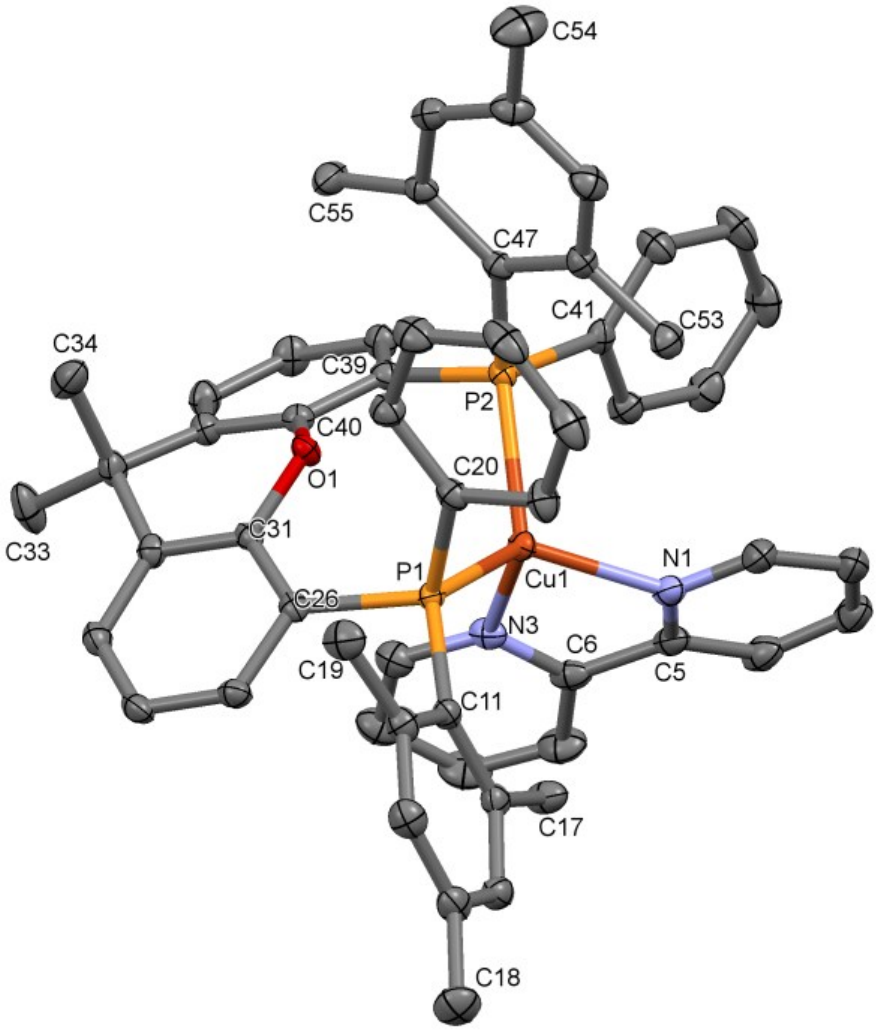


Fig. S13. Structure of the $[Cu(xantphosMes_2)(bpy)]^+$ cation in $[Cu(xantphosMes_2)(bpy)][PF_6]$ with ellipsoids plotted at 50% probability level; H atoms are omitted for clarity. Selected bond parameters: Cu1–P1 = 2.2808(6), Cu1–P2 = 2.3343(5), Cu1–N1 = 2.098(1), Cu1–N3 = 2.106(1) Å; P1–Cu1–P2 = 115.96(2), P1–Cu1–N1 = 128.48(4), P2–Cu1–N1 = 106.96(4), P1–Cu1–N3 = 112.79(4), P2–Cu1–N3 = 106.11(4), N1–Cu1–N3 = 79.08(6)°.

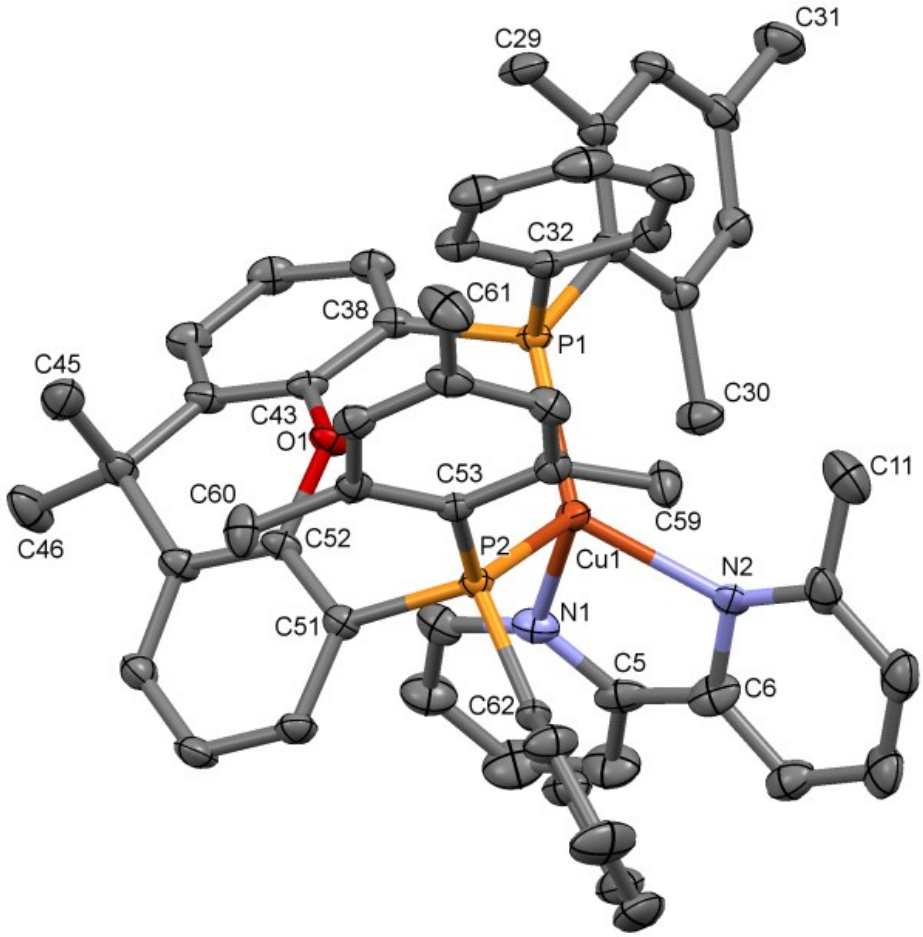


Fig. S14. Structure of one conformer of the $[Cu(xantphosMes_2)(6\text{-Mebpy})]^+$ cation in $[Cu(xantphosMes_2)(6\text{-Mebpy})][PF_6]$ with ellipsoids plotted at 50 % probability level; H atoms are omitted for clarity. The 6-Mebpy ligand is disordered and has been modelled over two sites, each with 50% occupany. Selected bond parameters for one conformer: Cu1–P1 = 2.2993(7), Cu1–P2 = 2.3718(8), Cu1–N1 = 2.070(3), Cu1–N2 = 2.182(3) Å; P1–Cu1–P2 = 115.25(3), P1–Cu1–N1 = 112.3(1), P2–Cu1–N1 = 104.7(1), P1–Cu1–N2 = 126.3(1), P2–Cu1–N2 = 111.6(1), N1–Cu1–N2 = 78.6(1)°. The values are similar for the second conformer.

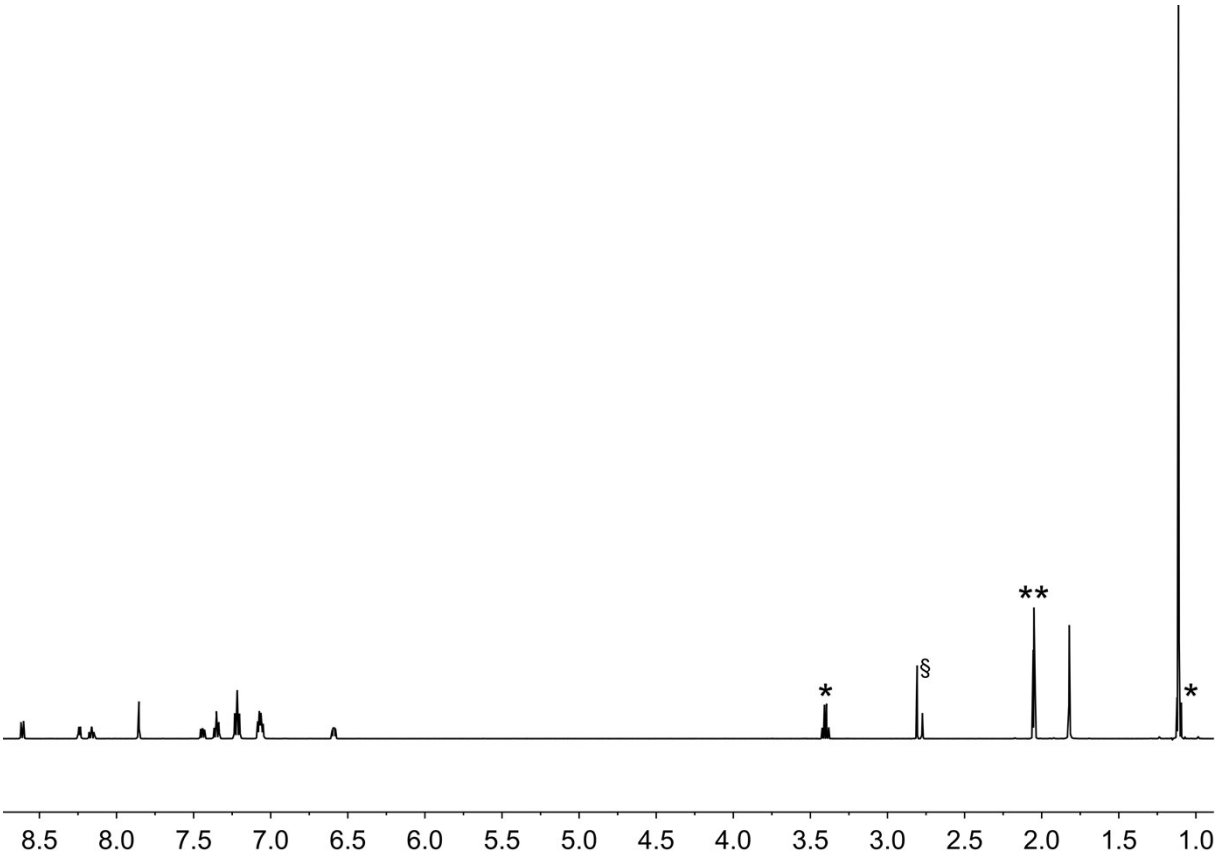


Fig. S15. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of [Cu(^{t}Bu$_2$xantphos)(bpy)][PF$_6$]. See Scheme 3 for atom labelling and Fig. 4 for expansion of the aromatic region. ** = residual acetone-d_5; * = Et_2O; § = H_2O and HOD.

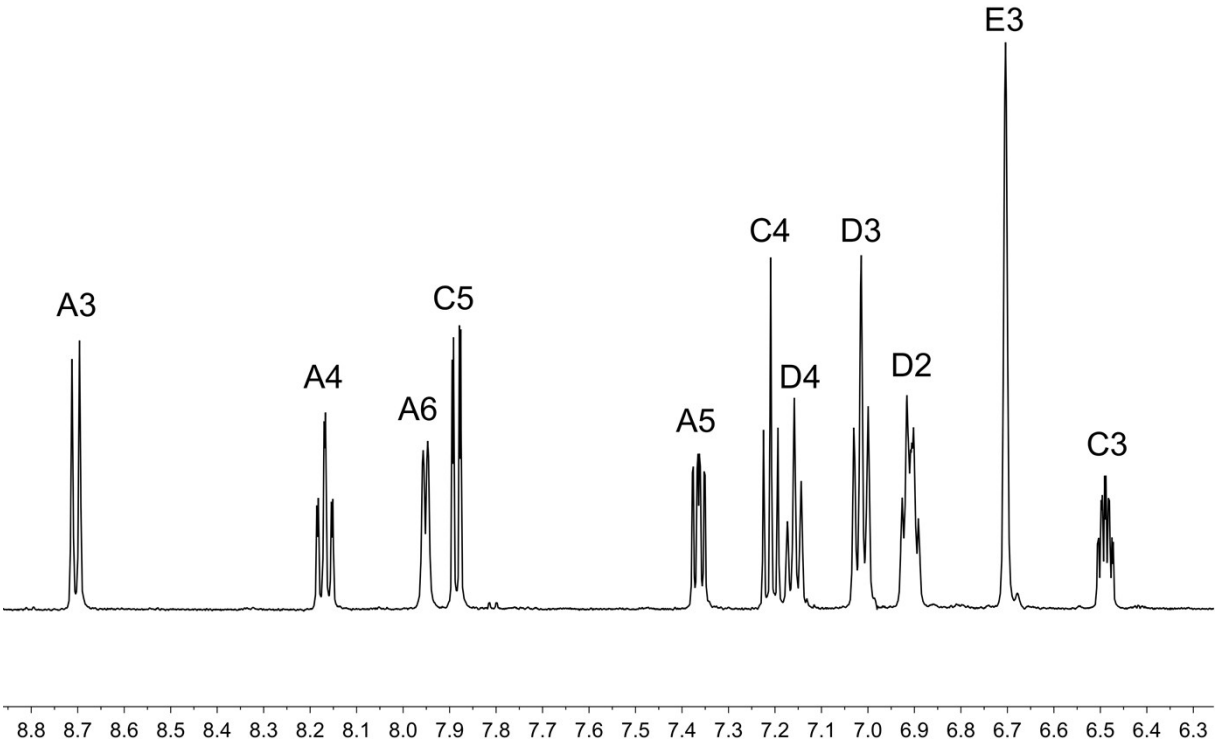


Fig. S16. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6) of [Cu(xantphosMes_2)(bpy)][PF_6]. See Scheme 3 for atom labelling.

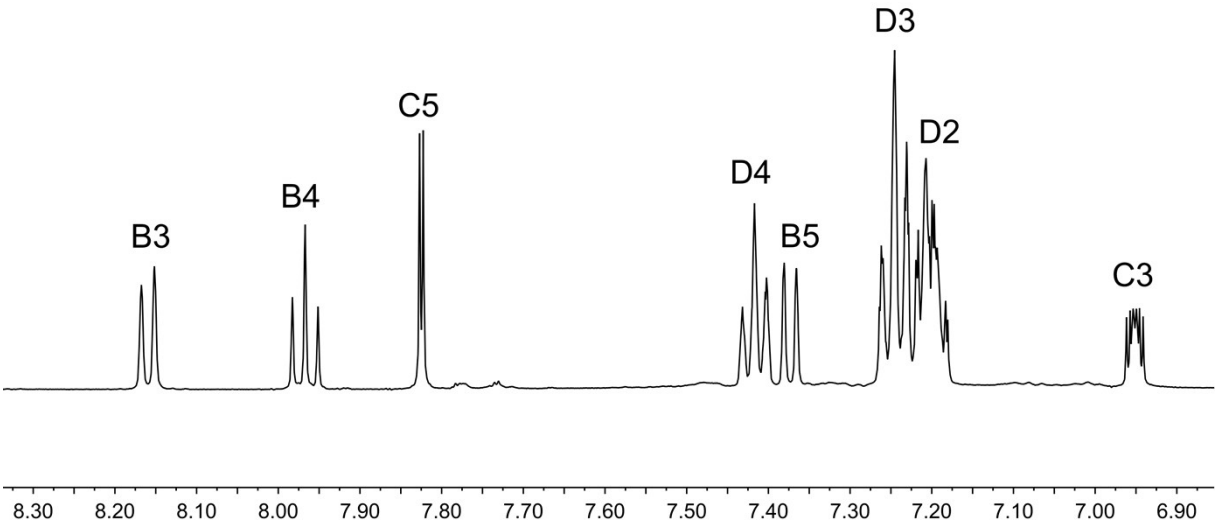


Fig. S17. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6) of [Cu($^{t}Bu_2$xantphos)(6,6'-Me_2bpy)][PF_6]. See Scheme 3 for atom labelling.

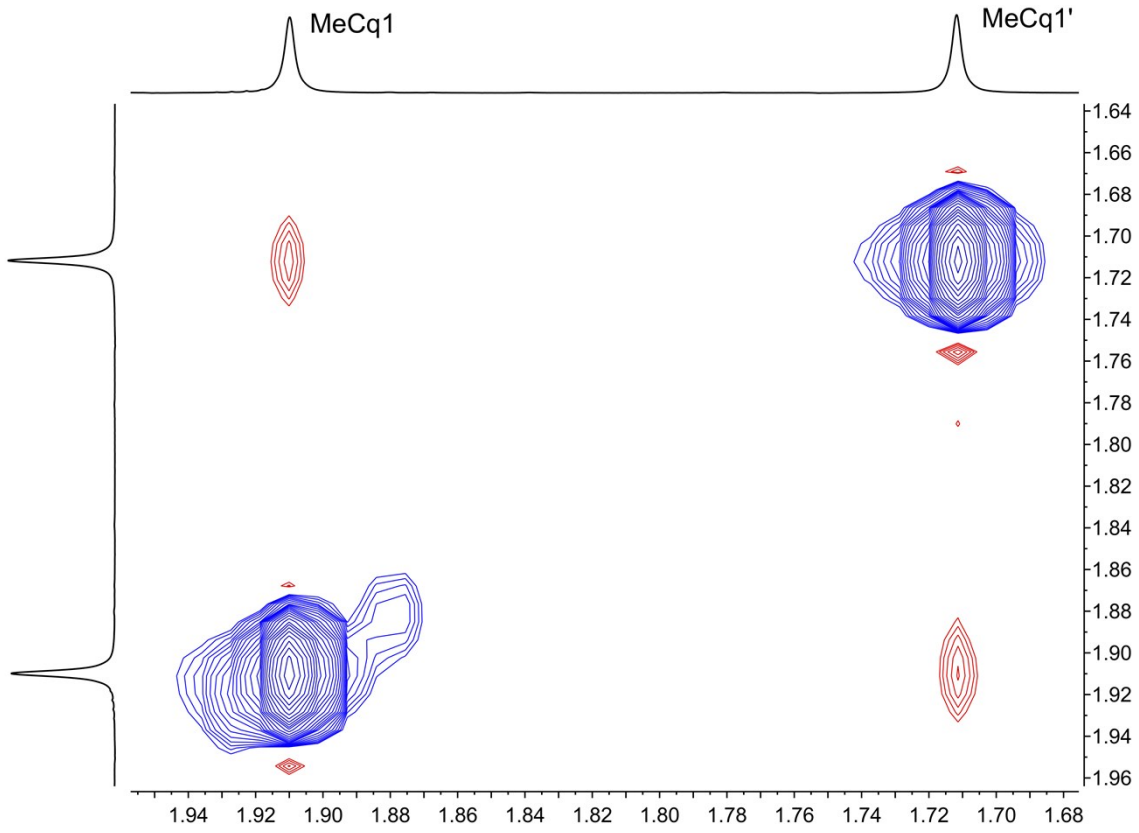


Fig. S18. Part of the NOESY spectrum (500 MHz, acetone-d_6) of [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF_6] showing NOESY peaks between the two xanthene methyl groups Cq1/Cq1'.

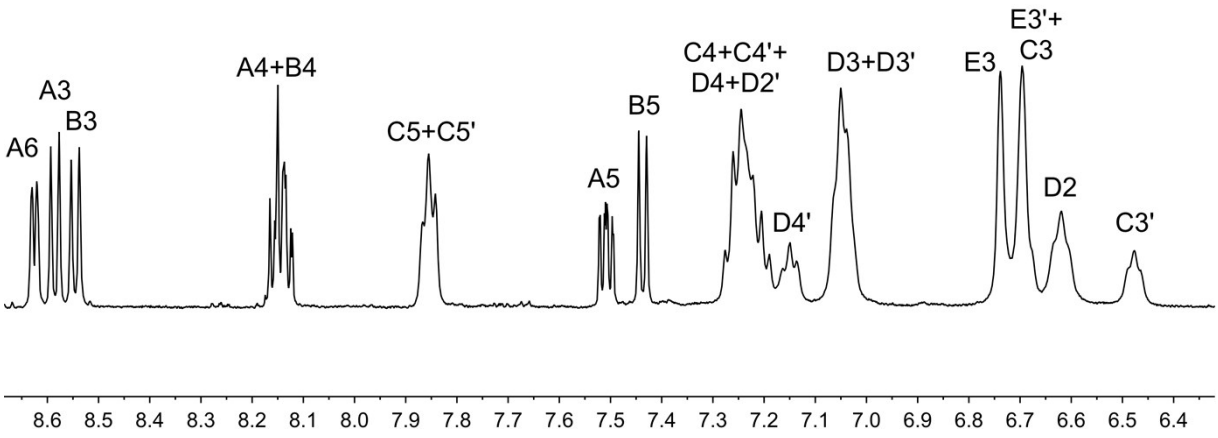


Fig. S19. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6) of [Cu(xantphosMes$_2$)(6-Mebpy)][PF_6]. See Scheme 3 for atom labelling.

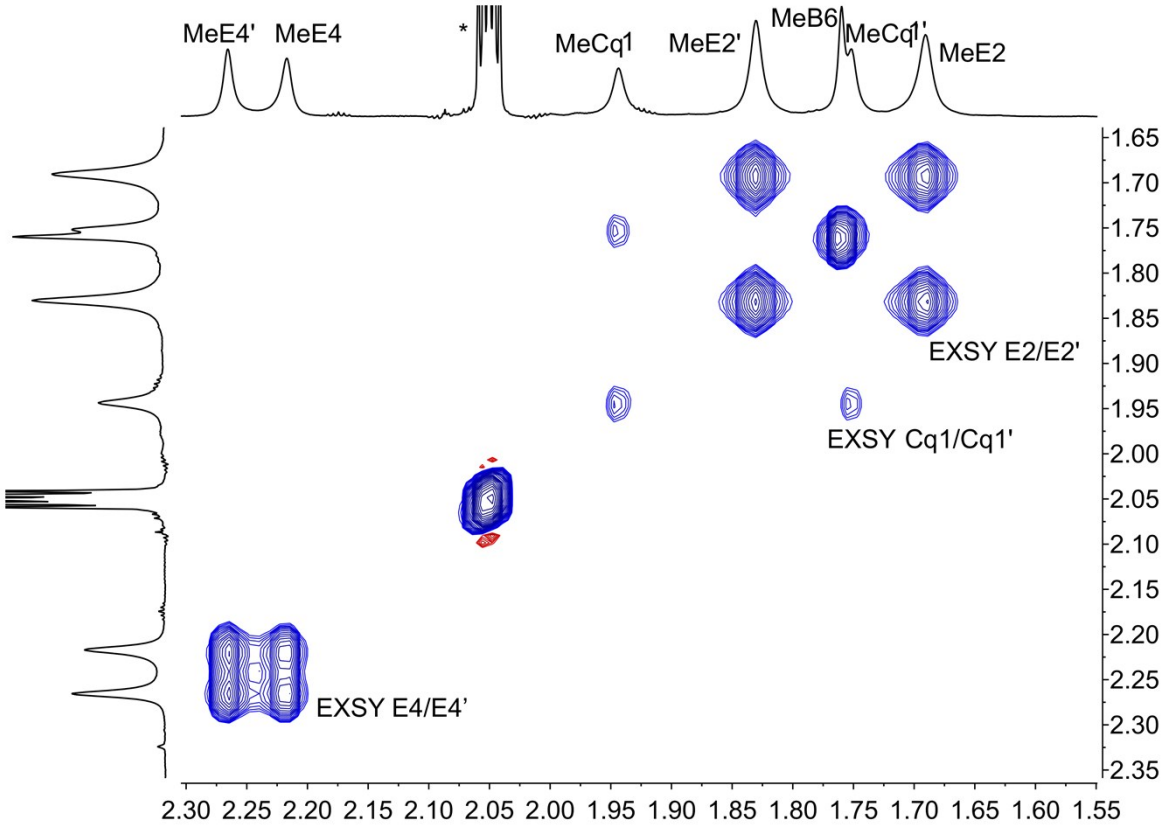


Fig. S20. Part of the NOESY spectrum (500 MHz, acetone-d_6) of [Cu(xantphosMes_2)(6-Mebpy)][PF_6] showing exchange (EXSY) peaks between pairs of mesityl methyl protons E2 and E2', E4/E4', and xanthene methyl protons Cq/Cq'. See Scheme 3 for atom labelling. * = residual acetone-d_5.

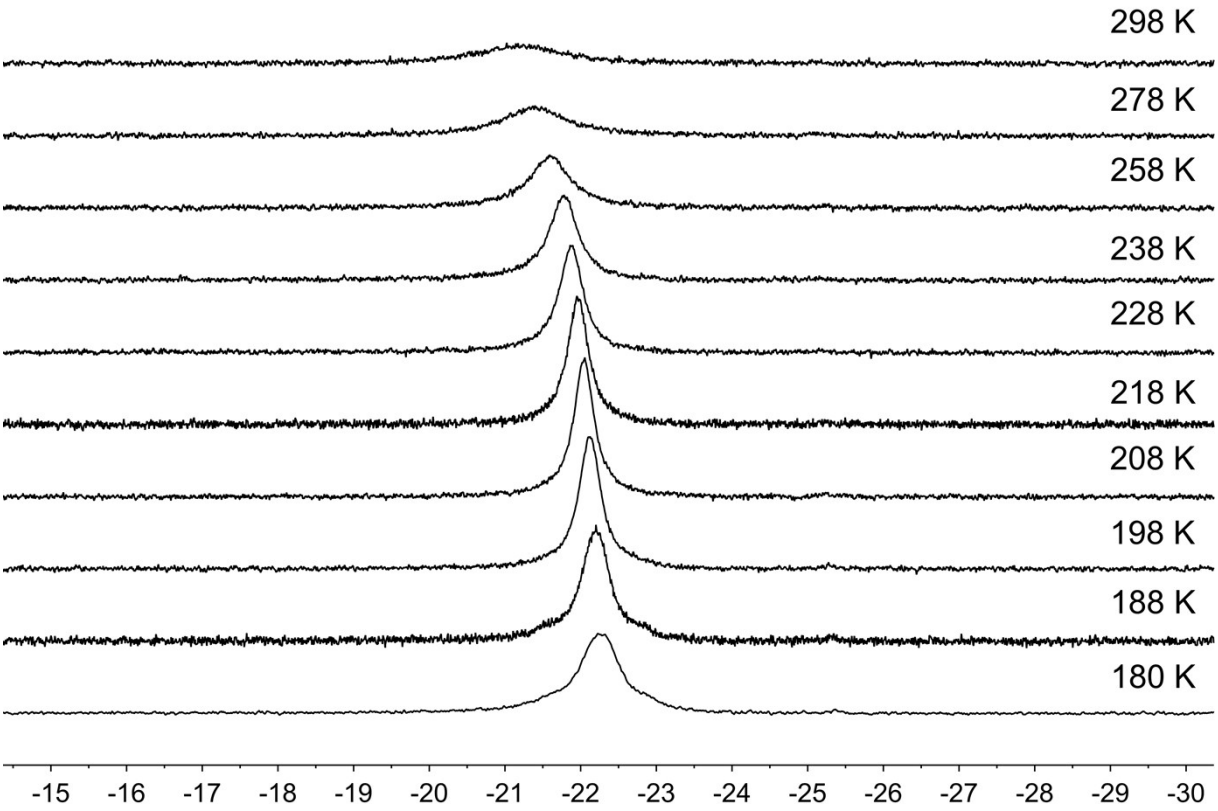


Fig. S21. Variable temperature ^{31}P NMR spectra (202 MHz, acetone-d_6) of [Cu(xantphosMes$_2$)(6-Mebpy)][PF_6]. The signal for the $[PF_6]^-$ was observed as a septet at δ – 144.6 ppm and was independent of temperature.

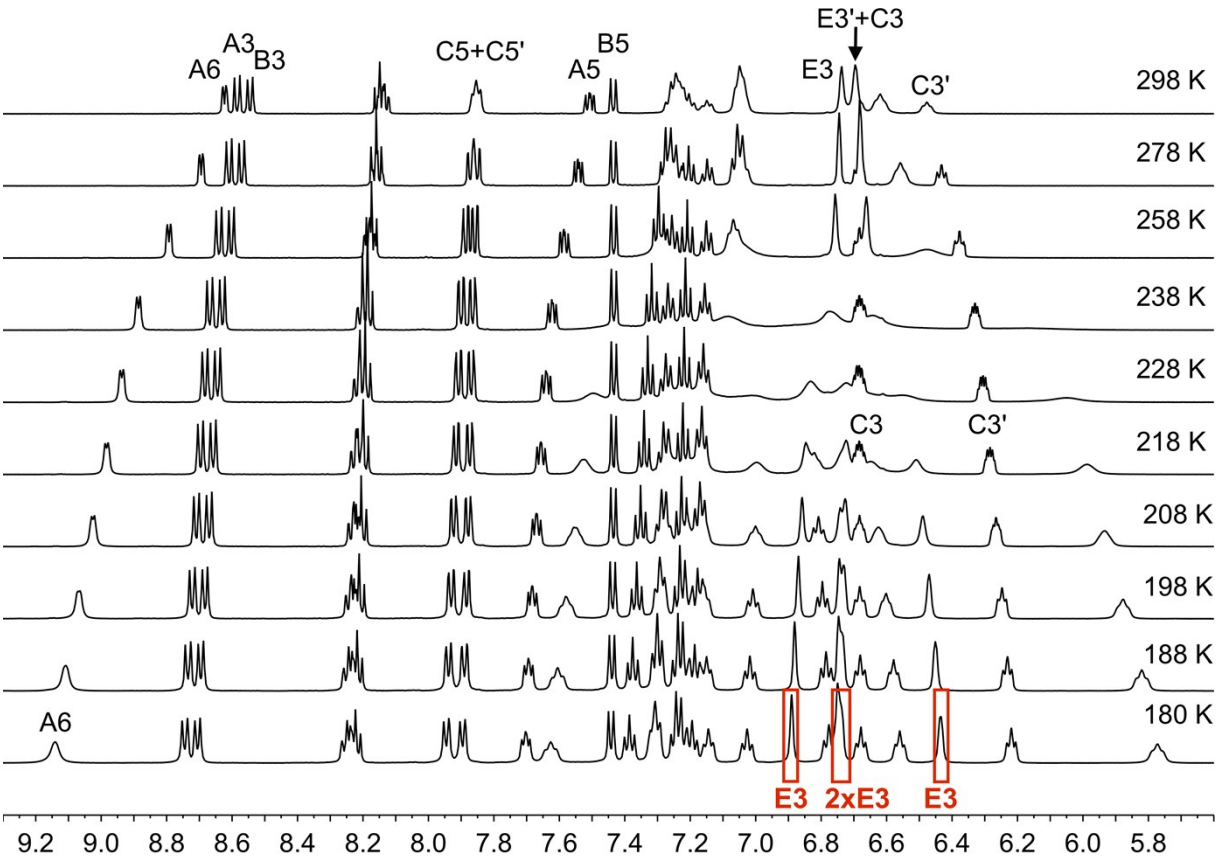


Fig. S22. Aromatic regions of the variable temperature ^{1}H NMR spectra (500 MHz, acetone-d_6) of [Cu(xantphosMes$_2$)(6-Mebpy)][PF$_6$]. See Scheme 3 for atom labelling. The red-highlighted signals at 180 K correspond to those assigned to the four independent mesityl E3 protons with rotation of the mesityl groups frozen out.

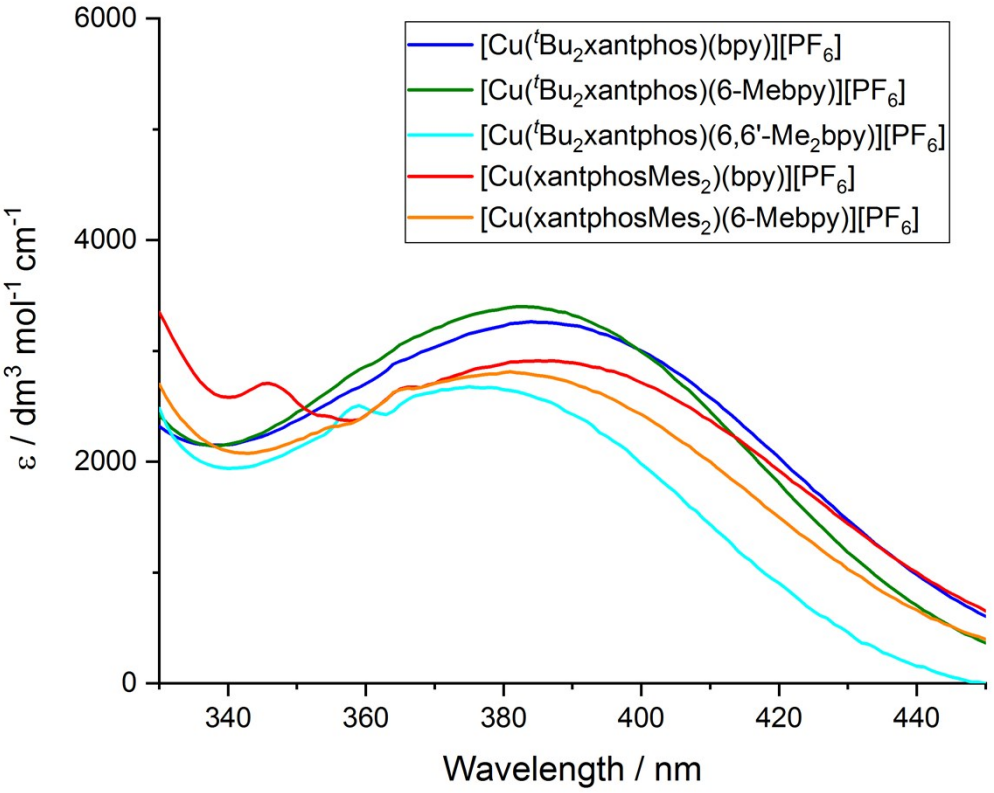


Fig. S23. Absorption spectra of [Cu(P^P)(N^N)][PF_6] complexes in CH_2Cl_2 at a concentration of 2.5 x 10^{-5} mol dm^{-3}.

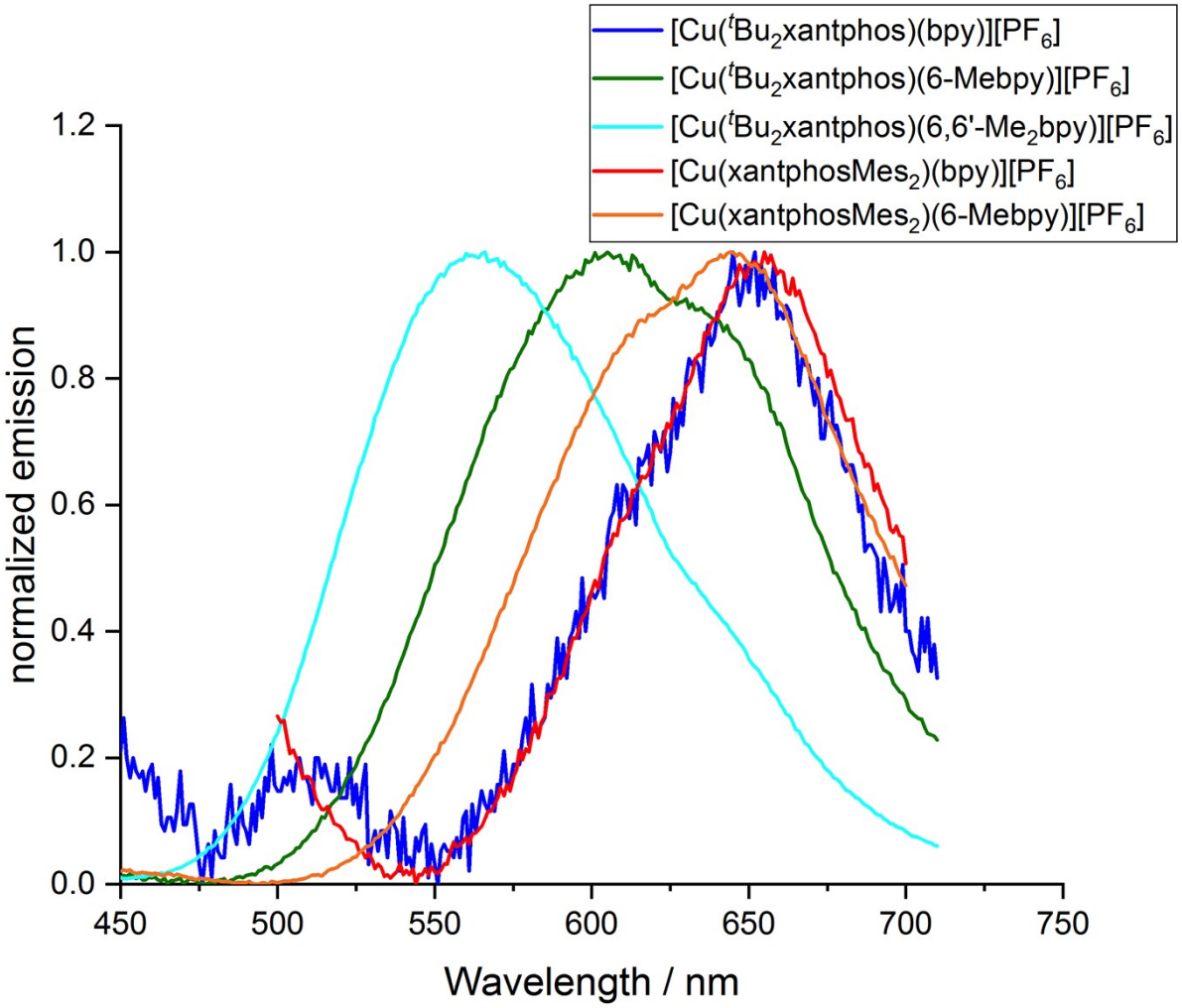


Fig. S24. Normalized solution emission spectra [Cu(P^P)(N^N)][PF_6] complexes in CH_2Cl_2 (λ_{exc} = 365 nm) at a concentration of 2.5 x 10^{-5} mol dm^{-3} for [Cu(^{t}Bu$_2$xantphos)(bpy)][PF_6], [Cu(^{t}Bu$_2$xantphos)(6-Mebpy)][PF_6] and [Cu(^{t}Bu$_2$xantphos)(6,6'-Me$_2$bpy)][PF_6] and 5.0 x 10^{-5} mol dm^{-3} for [Cu(xantphosMes$_2$)(bpy)][PF_6] and [Cu(xantphosMes$_2$)(6-Mebpy)][PF_6].

Table S1 Selected structural parameters calculated at the B3LYP-D3/(def2svp+def2tzvp) level in CH_2Cl_2 solution for $[Cu(P^P)(N^N)]^+$ complexes in their electronic ground state S_0 and in their first triplet excited state T_1.

Complex cation	Cu–P distance / Å (Cu1–P1; Cu1–P2)	Cu–N distance / Å (Cu1–N1; Cu1–N2)	P–Cu–P chelating angle / deg	N–Cu–N chelating angle / deg	Angle between P–Cu–P and N–Cu–N planes / deg	N–C–C–N torsion angle /deg
Ground State (S_0)						
$[Cu(xantphos)(bpy)]^{+a}$	2.269; 2.270	2.104; 2.068	114.40	79.75	86.94	3.23
$[Cu(^tBu_2xantphos)(bpy)]^+$	2.271; 2.274	2.119; 2.068	114.01	79.61	82.75	–9.79
$[Cu(^tBu_2xantphos)(6\text{-}Mebpy)]^+$	2.280; 2.281	2.100; 2.092	113.17	79.62	87.96	–1.94
$[Cu(^tBu_2xantphos)(6,6'\text{-}Me_2bpy)]^+$	2.272; 2.313	2.120; 2.118	118.83	79.44	86.12	8.62
$[Cu(xantphosMes_2)(bpy)]^+$	2.333; 2.356	2.156; 2.147	114.77	77.84	83.39	14.29
$[Cu(xantphosMes_2)(6\text{-}Mebpy)]^{+b}$	2.323; 2.365	2.152; 2.138	114.40	77.80	81.74	5.81
$[Cu(xantphosMes_2)(6\text{-}Mebpy)]^{+c}$	2.308; 2.371	2.138; 2.132	114.49	78.04	88.58	–0.06
Triplet Excited State (T_1)						
$[Cu(xantphos)(bpy)]^{+a}$	2.350; 2.399	1.997; 1.981	105.92	83.06	57.53	1.99
$[Cu(^tBu_2xantphos)(bpy)]^+$	2.354; 2.392	1.989; 1.969	105.64	83.29	57.18	3.15
$[Cu(^tBu_2xantphos)(6\text{-}Mebpy)]^+$	2.359; 2.379	1.992; 1.969	104.87	83.53	64.62	–3.15
$[Cu(^tBu_2xantphos)(6,6'\text{-}Me_2bpy)]^+$	2.381; 2.392	2.018; 1.981	106.82	83.84	70.68	–3.10
$[Cu(xantphosMes_2)(bpy)]^+$	2.398; 2.427	2.034; 1.968	105.92	82.85	65.14	–5.31
$[Cu(xantphosMes_2)(6\text{-}Mebpy)]^{+b}$	2.438; 2.474	2.074; 1.974	104.49	82.65	77.90	–4.63
$[Cu(xantphosMes_2)(6\text{-}Mebpy)]^{+c}$	2.408; 2.487	2.062; 1.991	103.62	81.86	64.59	8.44

[a] Values from ref. [3]. [b, c] Two different conformations were optimized for the $[Cu(xantphosMes_2)(6\text{-}Mebpy)]^+$ complex representing the two different conformers described in the "Single crystal structure Section" in the main text. The structure labelled with "b" is that with the methyl substituent of the 6-Mebpy ligand lying over the xanthene 'bowl', whereas the structure labelled with "c" is that where the methyl is remote from the xantphos. See the main text for more details about these structures.

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2 . B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, 1998, **120**, 3694.

3. S. Keller, A. Prescimone, H. Bolink, M. Sessolo, G. Longo, L. Martínez-Sarti, J. M. Junquera-Hernández, E. C. Constable, E. Ortí and C. E. Housecroft, *Dalton Trans.*, 2018, DOI: 10.1039/c8dt01338a.