Supporting Information

**Cu(I) Complexes of Multidentate \(N,C,N\)- and \(P,C,P\)-Carbodiphosphorane Ligands and their Photoluminescence**

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**Experimental Procedures**

All reactions were carried out under inert atmosphere using standard Schlenk techniques. Air or moisture sensitive substances were stored in a nitrogen-flushed glovebox. Solvents were purified according to common literature procedures\(^1\) and stored under an inert atmosphere over molecular sieve (3 Å or 4 Å). CDP(Py)\(^2\) and (CH\(_2\))(dppm)\(^3,4\) were synthesized according to the literature.

\(^1\)H, \(^13\)C and \(^{31}\)P NMR spectra were recorded on a Bruker Avance III HD 250, Avance II 300, Avance III HD 300 or Avance III HD 500 spectrometer at room temperature if not stated differed. Chemical shift \(\delta\) is denoted relatively to SiMe\(_4\) (\(^1\)H, \(^13\)C) or 85% H\(_3\)PO\(_4\) (\(^{31}\)P). \(^1\)H and \(^{13}\)C NMR spectra were referenced to the solvent signals.\(^5\) Multiplicity is abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). High-resolution mass spectrometry was performed on a Thermo Fisher Scientific LTQ-FT Ultra or a Jeol AccuTOF GCv., elemental analysis on an Elementar Vario Micro Cube. IR spectra and UV/Vis spectroscopy measurements were recorded in a glovebox on a Bruker Alpha ATR-FTIR and with an AvaLight-DHclight source and an AvaSpec-2048 detector using quartz cuvettes and dichloromethane as solvent. UV/Vis spectra were taken at different concentrations to calculate the molar extinction coefficient by using the Beer–Lambert law. Cyclic voltammetry measurements were carried out with an Ivium Technologies Iviumstat or a Metrohm AutolabPGSTAT204 using a RHD Instruments microcell HC under nitrogen at 25 °C. A platinum working electrode (diameter=0.25 mm) and a platinum counter electrode was used, as well as a silver/silver sulfide reference electrode. Ferrocene was used as internal standard. Dried\(^6\) DMSO from Sigma–Aldrich was used as solvent and tetrabutylammonium hexafluorophosphate (TBAPF\(_6\); ≥99.0 %, from Fluka) was used as electrolyte (50 mmol·L\(^{-1}\)) for electrochemical analysis.

**Synthesis**

\[
\begin{align*}
\text{[CuCl}_2\text{(CDP(Py)}_2\text{)] (2)}
\end{align*}
\]

A 446 mg portion (0.83 mmol, 1 eq.) of 1 and 164 mg (1.66 mmol, 2 eq.) of cupper(I) iodide were suspended in 15.0 ml THF at room temperature and stirred for 18 h. The solvent was then evaporated and the precipitate was washed with 5 · 15 ml of diethyl ether and 5 · 15 ml of pentane. The highly orange residue was dried in vacuo and collected in an 86% yield (523 mg, 0.71 mmol). \(^{31}\)P{H} NMR (CCl\(_2\)D\(_2\), 101 MHz): \(\delta\) 21.4 (s) ppm. \(^1\)H NMR (CCl\(_2\)D\(_2\), 300 MHz): \(\delta\) 8.84-8.83 (d, \(J_{H,H} = 4.5\) Hz, 2H, H\(_6\)), 7.77-7.72 (m, 2H, H\(_4\)), 7.70-7.63 (m, 8H, H\(_8\)), 7.54-7.50 (m, 2H, H\(_5\)), 7.44 (t, \(J_{H,H} = 7.6\) Hz, 4H, H\(_{10}\)), 7.37-7.34 (m, 2H, H\(_3\)), 7.25 (t, \(J_{H,H} = 7.55\) Hz, 8H, H\(_9\)) ppm. \(^{13}\)C NMR (CCl\(_2\)D, 75 MHz): \(\delta\)
155.0-153.8 (m, C2), 149.9 (t, $\frac{3}{J_{C,P}} = 1.73$ Hz, C6), 137.9 (t, $\frac{3}{J_{C,P}} = 5.03$ Hz, C4), 133.4 (t, $\frac{2}{J_{C,P}} = 4.97$ Hz, C8), 123.6 (s, C10), 129.1 (t, $\frac{2}{J_{C,P}} = 5.82$ Hz, C9), 128.8-127.8 (m, C7), 128.0 (m, C3), 126.8 (s, C5), -3.9 (m, C1) ppm. APCI-MS: $m/z$ 735.1 [M+H]$^+$. Elem. anal. (%) found C, 56.49; H, 3.92; N, 4.05; C35H28N2P2Cu2Cl2 required C, 57.07; H, 3.83; N, 3.80.

\[[(CuI)_2(CDP(Py)_2)](PF_6)_2 (3)\]

A 100 mg portion (0.19 mmol, 1 eq.) of 1 and 71 mg (0.37 mmol, 2 eq.) of copper(I) iodide were suspended in 5.0 ml THF at room temperature and stirred for 18 h. The solvent was then evaporated and the precipitate was washed with 5 · 5 ml of diethyl ether and 5 · 5 ml of pentane. The highly orange residue was dried in vacuo and collected in a 63% yield (107 mg, 0.12 mmol). $^{31}$P{H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 21.5 (s) ppm. H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 8.98-8.97 (d, $J_{HH} = 4.9$ Hz, 2H, H6), 7.79-7.75 (m, 2H, H4), 7.65-7.59 (m, 10H, H8, H5), 7.44 (t, $J_{HH} = 0.8$, 7.5 Hz, 4H, H10), 7.39-7.36 (m, 2H, H3), 7.26-7.3 (m, 8H, H9) ppm. $^{13}$C NMR (CCl$_2$D, 75 MHz): $\delta$ 150.9 (m, C6), 137.9 (t, $\frac{2}{J_{C,P}} = 5.5$ Hz, C4), 133.6 (t, $\frac{2}{J_{C,P}} = 4.9$ Hz, C8), 132.7 (s, C10), 129.3 (t, $\frac{2}{J_{C,P}} = 5.7$ Hz, C9), 128.7 (m, C7), 128.3 (s, C3), 127.2 (s, C5) ppm. Elem. anal. (%) found C, 45.52; H, 3.32; N, 3.25; C35H28N2P2Cu2Cl2 required C, 45.72; H, 3.07; N, 3.05.

\[[(CuPh)$\text{3}_{2}(CDP(Py))_{2}]$PF$_6_{2}$ (4)\]

A 50.0 mg portion (0.09 mmol, 1 eq.) of 1 and 69.2 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 48.7 mg portion (0.08 mmol, 2 eq.) of triphenylphosphine was added and the mixture stirred for additional 24 h. The solvent was then removed and the precipitate formed was washed with 2 · 5 ml of diethyl ether and 2 · 5 ml of pentane. The light yellow residue was dried in vacuo and collected in a 72% yield (100 mg, 0.07 mmol). $^{31}$P{H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 32.9 (s), 3.5 (s), 145.1 (sep.) ppm. H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 8.13 (t, $J_{HH} = 7.5$ Hz, 2H, CH$_{arom}$), 7.96 (d, $J_{HH} = 4.8$ Hz, 2H, CH$_{arom}$), 7.71-7.68 (m, 2H, CH$_{arom}$), 7.57 (t, $J_{HH} = 6.0$ Hz, 2H, CH$_{arom}$), 7.47 (q, $J_{HH} = 8.4$ Hz, 10H, CH$_{arom}$), 7.28-7.15 (m, 20H, CH$_{arom}$), 7.07 (t, $J_{HH} = 7.2$ Hz, 8H, CH$_{arom}$), 6.93 (dd, $J_{HH} = 7.4$, 11.3 Hz, 12H, CH$_{arom}$) ppm. $^{13}$C NMR (CCl$_2$D, 75 MHz): $\delta$ 151.3, 146.2, 141.0, 134.3, 133.9, 133.7, 133.2 (t, $\frac{2}{J_{C,P}} = 4.8$ Hz), 132.1, 130.8, 130.3, 130.2, 130.2, 130.1, 130.0, 129.5 ppm. Elem. anal. (%) found C, 56.36; H, 4.26; N, 1.92; C$_{71}$H$_{58}$N$_2$P$_6$Cu$_2$F$_{12}$ required C, 57.61; H, 3.95; N, 1.89. $\phi_{PL} = 36\%$. 

![Diagram](image-url)
[(Cu(PC$_8$H$_4$OMe)$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (5)

A 50.0 mg portion (0.09 mmol, 1 eq.) of 1 and 69.2 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 66.0 mg portion (0.18 mmol, 2 eq.) of tris(o-methoxyphenyl)phosphine was added and the mixture stirred for additional 24 h. The solvent was then removed and the precipitate formed was washed with 2 - 5 ml of diethyl ether and 2 - 5 ml of pentane. The light yellow residue was dried in vacuo and collected in a 47% yield (72.0 mg, 0.04 mmol). $^{31}$P{H} NMR (CCl$_4$D$_2$, 101 MHz): $\delta$32.8 (s), -0.3 (s), 144.5 (sep.) ppm. $^1$H NMR (CCl$_4$D$_2$, 300 MHz): $\delta$8.12-8.07 (m, 4H, $CH_{arom}$), 7.72-7.69 (m, 2H, $CH_{arom}$), 7.61 (t, $J_{H,H} = 5.7$ Hz, 2H, $CH_{arom}$), 7.47 (t, $J_{H,H} = 6.3$ Hz, 4H, $CH_{arom}$), 7.47 (q, $J_{H,H} = 8.4$ Hz, 10H, $CH_{arom}$), 7.28-7.27 (m, 8H, $CH_{arom}$), 7.12-7.08 (m, 8H, $CH_{arom}$), 6.87-6.81 (m, 12H, $CH_{arom}$), 6.64 d, $J_{H,H} = 7.7$ Hz, 2H, $CH_{arom}$), 3.79 (s, 18H, 6 $CH_2$) ppm. $^{13}$C NMR (CCl$_4$D$_2$, 75 MHz): $\delta$162.6, 151.4, 140.7, 135.3 (d, $J_{CP} = 16.1$ Hz), 134.2, 133.3 (t, $J_{CP} = 4.9$ Hz), 130.1 (t, $J_{CP} = 6.0$ Hz), 129.2, 122.4, 121.8, 115.6 (d, $J_{CP} = 11.2$ Hz), 56.1 ppm. Elem. anal. (%) found C, 57.98; H, 4.29; N, 1.89; C$_{77}$H$_{70}$N$_2$P$_6$O$_6$Cu$_2$F$_{12}$ required C, 57.07; H, 3.78; N, 1.87.

![Chemical structure](image)

$[\text{Cu}_2(\text{DPEPhos})(\text{CDP(Py)}_2)](\text{PF}_6)_2$ (6)

A 50.0 mg portion (0.09 mmol, 1 eq.) of 1 and 69.2 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 50.0 mg portion (0.09 mmol, 1 eq.) of bis[(2-diphenylphosphino)phenyl] ether was added and the mixture stirred for additional 24 h. The solvent was then removed and the precipitate formed was washed with 2 - 5 ml of diethyl ether and 2 - 5 ml of pentane. The light yellow residue was dried in vacuo and collected in an 86% yield (120.0 mg, 0.08 mmol). $^{31}$P{H} NMR (CCl$_4$D$_2$, 101 MHz): $\delta$29.7 (s), -8.7 (s), 144.5 (sep.) ppm. $^1$H NMR (CCl$_4$D$_2$, 300 MHz): $\delta$8.05-7.99 (m, 2H, $CH_{arom}$), 7.83-7.79 (m, 2H, $CH_{arom}$), 7.71-7.64 (m, 4H, $CH_{arom}$), 7.55-7.51 (m, 2H, $CH_{arom}$), 7.46-7.34 (m, 12H, $CH_{arom}$), 7.30-7.26 (m, 4H, $CH_{arom}$), 7.21-7.06 (m, 18H, $CH_{arom}$), 6.91-6.75 (m, 10H, $CH_{arom}$), 6.70-6.65 (m, 2H, $CH_{arom}$). Elem. anal. (%) found C, 56.42; H, 4.06; N, 1.51; C$_{71}$H$_{56}$N$_2$P$_6$Cu$_2$F$_{12}$O required C, 56.13; H, 4.53; N, 1.66.
[Cu$_2$(XantPhos)(CDP(Py)$_2$)](PF$_6$)$_2$ (7)

A 50.0 mg portion (0.09 mmol, 1 eq.) of 1 and 69.9 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 53.7 mg portion (0.09 mmol, 1 eq.) of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene was added and the mixture stirred for additional 24 h. The solvent was then removed and the precipitate formed was washed with 2·5 ml of diethyl ether and 2·5 ml of pentane. The light yellow residue was dried in vacuo and collected in an 81% yield (93.0 mg, 0.08 mmol). $^{31}$P{H} NMR (CCl$_4$, 101 MHz): δ 34.9 (s), –6.1 (s), 143.8 (sep.) ppm. $^1$H NMR (CCl$_4$, 300 MHz): δ 8.13 (d, $J_{H,H}$ = 4.6 Hz, 2H, CH$_{arom}$), 7.98 (t, $J_{H,H}$ = 7.0 Hz, 2H, CH$_{arom}$), 7.64 (d, $J_{H,H}$ = 6.8 Hz, 2H, CH$_{arom}$), 7.54–7.43 (m, 10H, CH$_{arom}$), 7.43 (br.s, 2H, CH$_{arom}$), 7.19–7.07 (m, 22H, CH$_{arom}$), 6.78 (br.s, 10H, CH$_{arom}$), 6.40 (t, $J_{H,H}$ = 8.3 Hz, 2H, CH$_{arom}$), 1.65 (s, 6H, 2·CH$_3$). $^{13}$C NMR (CCl$_4$, 75 MHz): δ 156.2, 155.5, 151.6 (d, $^2$J$_{C,P}$ = 8.8 Hz), 151.3 (t, $^2$J$_{C,P}$ = 6.7 Hz), 140.3 (t, $^2$J$_{C,P}$ = 4.7 Hz), 134.2, 133.9 (t, $^2$J$_{C,P}$ = 7.5 Hz), 133.7, 133.4, 133.1, 132.3, 131.0, 130.4, 130.3, 130.1 (d, $^2$J$_{C,P}$ = 10.1 Hz), 129.8, 129.4, 129.0, 125.1 (d, $^2$J$_{C,P}$ = 6.1 Hz), 118.0, 117.7, 34.8, 33.4 ppm. Elem. anal. (%) found C, 57.01; H, 4.16; N, 2.09; C$_{74}$H$_{60}$N$_2$P$_6$Cu$_2$F$_{12}$O$_2$ required C, 57.93; H, 3.94; N, 1.83.

[Cu$_2$(dpff)(CDP(Py)$_2$)](PF$_6$)$_2$ (8)

A 50.0 mg portion (0.09 mmol, 1 eq.) of 1 and 69.9 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 51.5 mg portion (0.09 mmol, 1 eq.) of 1,1’-bis(diphenylphosphino)ferrocene was added and the mixture stirred for additional 24 h. The solvent was then removed and the precipitate formed was washed with 2·5 ml of diethyl ether and 2·5 ml of pentane. The light yellow residue was dried in vacuo and collected in a 90% yield (102.0 mg, 0.08 mmol). $^{31}$P{H} NMR (CCl$_4$, 101 MHz): δ 36.5 (s), –3.1 (s), 143.9 (sep.) ppm. $^1$H NMR (CCl$_4$, 300 MHz): δ 8.33 (d, $J_{H,H}$ = 4.8 Hz, 2H, CH$_{arom}$), 8.27 (t, $J_{H,H}$ = 6.9 Hz, 2H, CH$_{arom}$), 7.83–7.79 (m, 4H, CH$_{arom}$), 7.53–7.17 (m, 30H, CH$_{arom}$), 7.00 (br.s, 8H, CH$_{arom}$), 4.45–4.21 (m, 10H, CpH) ppm. $^{13}$C NMR (CCl$_4$, 75 MHz): δ 155.9, 151.9, 140.9, 134.2, 133.1, 131.7, 130.3 (t, $^2$J$_{C,P}$ = 5.9 Hz), 129.6, 73.8, 73.1, 72.2, 71.8 ppm. Elem. anal. (%) found C, 53.26; H, 3.83; N, 1.98; C$_{69}$H$_{56}$N$_2$P$_6$Cu$_2$F$_{12}$Fe required C, 53.78; H, 3.76; N, 1.98.
A 23.0 mg portion (0.14 mmol, 2 eq.) of carbazole (10) and 13.0 mg (0.14 mmol, 2 eq.) of sodium tert-butoxide were treated with 2.0 ml THF at room temperature and stirred for 3 h. A suspension of 50.0 mg of [(CuCl)$_2$(CDP(Py)$_2$) (2, 0.07 mmol, 1 eq.) in 2.0 ml THF was added and the reaction mixture stirred for additional 70 h at room temperature. The solvent was then removed and the precipitate formed was washed with 3 · 5 ml of diethyl ether and 3 · 5 ml of pentane. The light orange residue was dried in vacuo and collected in a 56% yield (38.0 mg, 0.04 mmol). $^{31}$P{H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 22.8 ppm. $^1$H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 8.50 (d, $J_{HH} = 4.7$ Hz, 2H, H6), 7.97 (dd, $J_{HH} = 0.4$, 7.5 Hz, 4H, H11), 7.94 (ddd, $J_{HH} = 1.1$, 8.3, 12.3 Hz, 8H, H8), 7.60 (ddt, $J_{HH} = 1.8$, 4.9, 7.7 Hz, 2H, H4), 7.42 (t, $J_{HH} = 7.4$ Hz, 4H, H10), 7.34-7.30 (m, 4H, H5, H3), 7.22-7.18 (m, 12H, H9, H12), 6.95 (dt, $J_{HH} = 1.3$, 7.0 Hz, 4H, H13), 6.95 (dt, $J_{HH} = 0.9$, 7.3 Hz, 4H, H14) ppm. $^{13}$C NMR (CCl$_2$D, 75 MHz): $\delta$ 155.4-154.2 (m, C2), 151.2 (s, C16), 150.6 (t, $J_{CP} = 8.3$ Hz, C6), 137.9 (t, $J_{CP} = 5.1$ Hz, C4), 133.8 (t, $J_{CP} = 4.8$ Hz, C8), 132.8 (s, C10), 129.3 (t, $J_{CP} = 5.9$ Hz, C9), 128.6-127.7 (m, C3, C7), 126.7 (s, C5), 124.5 (s, C15), 123.5 (s, C13), 119.6 (s, C11), 115.3 (s, C12), 114.9 (s, C13), −0.9 (t, $J_{CP} = 54.0$ Hz, C1) ppm. LIFDI-HRMS: m/z 539.18016. [M-H]$^+$: Elem. anal. (%) found C, 70.68; H, 4.44; N, 5.61; C$_{59}$H$_{44}$N$_4$P$_2$Cu$_2$ required C, 71.00; H, 4.66; N, 5.01.

A 76.0 mg portion (0.14 mmol, 1 eq.) of 1 and 74.0 mg (0.28 mmol, 2 eq.) of cupper(I) pentfluorothiophenolate were suspended in 5.0 ml THF at room temperature and stirred for 18 h. The solvent was then evaporated and the precipitate was washed with 5 · 15 ml of diethyl ether and 5 · 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 27% yield (40.0 mg, 0.04 mmol). $^{31}$P{H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 23.1 ppm. $^1$H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 8.81-8.66 (m, 2H, $CH_{arom}$), 7.94-7.87 (m, 5H, $CH_{arom}$), 7.72-7.66 (m, 2H, $CH_{arom}$), 7.60-7.47 (m, 10H, $CH_{arom}$), 7.46-7.40 (m, 4H,
CH\textsubscript{arom}), 7.27-7.12 (m, 5H, CH\textsubscript{arom}) ppm. Elem. anal. (%) found C, 42.47; H, 2.24; N, 2.28; C\textsubscript{47}H\textsubscript{28}P\textsubscript{4}F\textsubscript{22}N\textsubscript{2}S\textsubscript{2} required C, 41.70; H, 2.08; N, 2.07.

\[
\begin{align*}
\text{(CDP(CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}) (13)}
\end{align*}
\]

A 250.0 mg portion (0.30 mmol, 1.0 eq.) of [CH(dppm)\textsubscript{2}]Cl\textsuperscript{3+} (12) and 80.4 mg NaNH\textsubscript{2} (2.1 mmol, 6.5 eq.) were suspended in NH\textsubscript{3} (l) at \(-78^\circ\text{C}\) and stirred till the temperature reached room temperature, causing the NH\textsubscript{3} to vaporize. The light yellow residue was dissolved in toluene and the feed was removed via filtration. The solvent was then evaporated and the precipitate was washed with 2 \cdot 15 ml of pentane. The yellow residue was dried in vacuo and collected in a 98% yield (233.1 mg, 0.30 mmol). \textsuperscript{31}P\{H\} NMR (CDCl\textsubscript{3}, 101 MHz): \(\delta = 23.2\) (dt, \(J = 8.0, 14.7\) Hz), \(\delta = 15.8\) (d, \(J = 118.5\) Hz) ppm. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 7.09-7.71\) (m, 8H, CH\textsubscript{arom}), 7.51-7.31 (m, 8H, CH\textsubscript{arom}), 7.08-6.88 (m, 24H, CH\textsubscript{arom}), 3.44 (br.s, 3H, CH\textsubscript{2}), 1.44 (s, 1H, CH) ppm. APCI-HRMS: \(m/z\) 781.24799 [M+H]\textsuperscript{+}. Elem. anal. (%) found C, 77.99; H, 5.74; C\textsubscript{51}H\textsubscript{44}P\textsubscript{4} required C, 78.45; H, 5.68.

\[
\begin{align*}
\text{[(CuCl)\textsubscript{2}(CDP(CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2})] (14)}
\end{align*}
\]

A 50.0 mg portion (0.06 mmol, 1 eq.) of 13 and 12.9 mg (0.12 mmol, 2 eq.) of cupper(I) chloride were suspended in 5.0 ml THF at room temperature and stirred for 1 h. The solvent was then evaporated and the precipitate was washed with 3 \cdot 15 ml of diethyl ether and 2 \cdot 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 77% yield (48.1 mg, 0.05 mmol). \textsuperscript{31}P\{H\} NMR (CDCl\textsubscript{3}, 101 MHz): \(\delta = 20.4\) (dd, \(J = 34.6, 49.9\) Hz), \(\delta = 32.5\) (m) ppm. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 7.45\) (m, 18H, CH\textsubscript{arom}), 7.18 (m, 16H, CH\textsubscript{arom}), 6.95 (m, 6H, CH\textsubscript{arom}), 6.79 (br.s, 6H, CH\textsubscript{arom}), 4.06 (br.s, 4H, 2 \cdot CH\textsubscript{2}) ppm. APCI-HRMS: \(m/z\) 941.07087 [M-CI]\textsuperscript{+}.

\[
\begin{align*}
\text{[(CuI)\textsubscript{2}(CDP(CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2})] (15)}
\end{align*}
\]

A 50.0 mg portion (0.06 mmol, 1 eq.) of 13 and 24.5 mg (0.12 mmol, 2 eq.) of cupper(I) iodide were suspended in 5.0 ml THF at room temperature and stirred for 2 h. The solvent was then evaporated and the precipitate was washed with 3 \cdot 15 ml of diethyl ether and 2 \cdot 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 77% yield (23.3 mg, 0.03 mmol). \textsuperscript{31}P\{H\} NMR (CDCl\textsubscript{3}, 101 MHz): \(\delta = 20.4\) (m) ppm. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 7.18\) (m, 16H, CH\textsubscript{arom}), 7.17 (m, 12.9 mmol, 2 eq.) of cupper(I) chloride were suspended in 5.0 ml THF at room temperature and stirred for 1 h. The solvent was then evaporated and the precipitate was washed with 3 \cdot 15 ml of diethyl ether and 2 \cdot 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 98% yield (233.1 mg, 0.30 mmol). \textsuperscript{31}P\{H\} NMR (CDCl\textsubscript{3}, 101 MHz): \(\delta = 23.2\) (dt, \(J = 8.0, 14.7\) Hz), \(\delta = 15.8\) (d, \(J = 118.5\) Hz) ppm. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta = 7.09-7.71\) (m, 8H, CH\textsubscript{arom}), 7.51-7.31 (m, 8H, CH\textsubscript{arom}), 7.08-6.88 (m, 24H, CH\textsubscript{arom}), 3.44 (br.s, 3H, CH\textsubscript{2}), 1.44 (s, 1H, CH) ppm. APCI-HRMS: \(m/z\) 781.24799 [M+H]\textsuperscript{+}. Elem. anal. (%) found C, 77.99; H, 5.74; C\textsubscript{51}H\textsubscript{44}P\textsubscript{4} required C, 78.45; H, 5.68.
collected in a 83% yield (62.0 mg, 0.05 mmol). $^{31}$P{$^1$H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 22.2 (dd, $J = 36.9, 55.4$ Hz), $\sim$37.6--38.2 (m) ppm. $^{31}$P{$^1$H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 22.5 (m), $\sim$38.0 (m) ppm. $^1$H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 7.72-7.31 (m, 16H, $CH_{arom}$), 7.17-6.70 (m, 24H, $CH_{arom}$), 6.79 (br.s, 6H, $CH_{arom}$), 4.19 (br.s, 4H, 2 $CH_2$) ppm. APCI-HRMS: $m/z$ 1160.9147 [M+H]$^+$, 971.0806 [M-Cu+H]$^+$, 781.2461 [M-(Cu)$_2$+H]$^+$.

[(CuSPh)$_2$(CDP(CH$_2$PPh$_2$)$_2$)] (16)

A 58.0 mg portion (0.07 mmol, 1 eq.) of 13 and 26.0 mg (0.15 mmol, 2 eq.) of cupper(I) thiophenolate were suspended in 5.0 ml THF at room temperature and stirred for 42 h. The solvent was then evaporated and the precipitate was washed with 3 $\cdot$ 15 ml of diethyl ether and 2 $\cdot$ 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 52% yield (58.0 mg, 0.04 mmol). $^{31}$P{$^1$H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 19.8-19.0 (m), $\sim$33.1--33.9 ppm. $^1$H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 7.45-7.30 (m, 22H, $CH_{arom}$), 7.16-7.05 (m, 10H, $CH_{arom}$), 6.97-6.92 (m, 12H, $CH_{arom}$), 6.79 (br.s, 6H, $CH_{arom}$), 4.11 (br.s, 4H, 2 $CH_2$) ppm.

[CuCl(CDPH(CH$_2$PPh$_2$)$_2$)]PF$_6$ (17)

A 57.2 mg portion (0.07 mmol, 1 eq.) of 13 and 27.2 mg (0.07 mmol, 1 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were suspended in 5.0 ml DCM at room temperature and stirred for 12 h. The solvent was then evaporated and the precipitate was washed with 3 $\cdot$ 15 ml of diethyl ether and 2 $\cdot$ 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 74% yield (55.2 mg, 0.05 mmol). $^{31}$P{$^1$H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 20.8-19.2 (m), $\sim$29.6--30.4 (m), $\sim$32.0--33.0 (m) ppm. $^{19}$F{$^1$H} NMR (CCl$_2$D$_2$, 282 MHz): $\delta$ 71.7 (d, $J = 711$ Hz).

[CuPPh$_3$(CH(PPh$_2$CHPPh$_2$)$_2$)] (18)

A solution of 100 mg of [CH(dppm)$_2$]Cl (12) (0.12 mmol, 1 eq.) in 10 ml of THF was treated with 1.0 ml of $^6$BuLi in hexane (2.5 m, 0.24 mmol, 2.0 eq.) at $-78 ^\circ$C, while stirring. The reaction mixture was allowed to reach room temperature before a 55.7 mg portion (0.24, 2.0 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate was added. After stirring for an additional 1 h a 64.2 mg portion (0.24, 2.0 eq.) of
triphenylphosphine was added and the mixture stirred for additional 15 h. The solvent was then removed and the precipitate formed was washed with 2 \cdot 5 ml of diethyl ether and 2 \cdot 5 ml of pentane. The light yellow residue was dried in vacuo and collected in a 73% yield (98.0 mg, 0.08 mmol). $^{31}$P{H} NMR (CCl$_2$D$_2$, 101 MHz): $\delta$ 23.6 (d, $J_{P,P} = 142.2$ Hz), 14.4 (d, $J_{P,P} = 118.7$ Hz), $-$15.6 (d, $J_{P,P} = 142.2$ Hz) ppm. $^1$H NMR (CCl$_2$D$_2$, 300 MHz): $\delta$ 7.70-7.64 (m, 4H, CH$_{arom}$), 7.55-7.38 (m, 6H, CH$_{arom}$), 7.34-7.12 (m, 16H, CH$_{arom}$), 7.09-6.99 (m, 10H, CH$_{arom}$), 6.97-6.42 (m, 20H, CH$_{arom}$), 2.24 (t, $J_{P,H} = 8.2$ Hz, 1H, CH), 1.66-1.61 (m, 2H, 2 \cdot CH) ppm. Elem. anal. (%) found C, 74.67; H, 5.19; C$_{69}$H$_{59}$P$_5$Cu required C, 74.89; H, 5.37.

**NMR spectroscopy**

\[\left[\text{(CuCl)}_2\text{(CDP(Py)$_2$)}\right] (2)\]

![Figure S-1. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of $\left[\text{(CuCl)}_2\text{(CDP(Py)$_2$)}\right] (2)$.](image-url)
Figure S-2. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuCl)$_2$(CDP(Py)$_2$)] (2).

Figure S-3. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [(CuCl)$_2$(CDP(Py)$_2$)] (2).
$[(\text{CuI})_2(\text{CDP(Py)_2})]$ (3)

Figure S-4. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of $[(\text{CuI})_2(\text{CDP(Py)_2})]$ (3).
Figure S-5. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuI)$_2$(CDP(Py)$_2$)] (3).

Figure S-6. $^1$H NMR (CCl$_2$D$_2$, 200 K, 300 MHz, [ppm]) of [(CuI)$_2$(CDP(Py)$_2$)] (3).

Figure S-7. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [(CuI)$_2$(CDP(Py)$_2$)] (3).
\[(\text{CuPPh}_3)_2(\text{CDP(Py)_2})](\text{PF}_6)_2 \text{ (4)}\]

**Figure S-8.** $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of \([(\text{CuPPh}_3)_2(\text{CDP(Py)_2})](\text{PF}_6)_2 \text{ (4)}\).

**Figure S-9.** $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of \([(\text{CuPPh}_3)_2(\text{CDP(Py)_2})](\text{PF}_6)_2 \text{ (4)}\).
Figure S-10. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (4).

$[(\text{Cu(PPhOMe)}_3)_2\text{(CDP(Py)$_2$)}](\text{PF}_6)_2$ (5)

Figure S-11. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of $[(\text{Cu(PPhOMe)}_3)_2\text{(CDP(Py)$_2$)}](\text{PF}_6)_2$ (5).
Figure S-12. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(Cu(PPhOMe)$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (5).

Figure S-13. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [(Cu(PPhOMe)$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (5).
$[\text{Cu}_2(\text{DPEPhos})(\text{CDP(Py)}_2)](\text{PF}_6)_2$ (6)

**Figure S-14.** $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of $[\text{Cu}_2(\text{DPEPhos})(\text{CDP(Py)}_2)](\text{PF}_6)_2$ (6).

**Figure S-15.** $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of $[\text{Cu}_2(\text{DPEPhos})(\text{CDP(Py)}_2)](\text{PF}_6)_2$ (6).
[Cu₂(XantPhos)(CDP(Py)₂)](PF₆)₂ (7)

Figure S-16. ³¹P NMR (CCl₂D₂, 101 MHz, [ppm]) of [Cu₂(XantPhos)(CDP(Py)₂)](PF₆)₂ (7).

Figure S-17. ¹H NMR (CCl₂D₂, 300 MHz, [ppm]) of [Cu₂(XantPhos)(CDP(Py)₂)](PF₆)₂ (7).
Figure S-18. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [Cu$_2$(XantPhos)(CDP(Py)$_2$)](PF$_6$)$_2$ (7).

[Cu$_2$(dpff)(CDP(Py)$_2$)](PF$_6$)$_2$ (8)

Figure S-19. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [Cu$_2$(dpff)(CDP(Py)$_2$)](PF$_6$)$_2$ (8).
Figure S-20. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [Cu$_2$(dppf)(CDP(Py)$_2$)](PF$_6$)$_2$ (8).

Figure S-21. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [Cu$_2$(dppf)(CDP(Py)$_2$)](PF$_6$)$_2$ (8).
[(CuCarb)$_2$(CDP(Py)$_2$)] (11)

Figure S-22. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (11).

Figure S-23. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (11).
Figure S-24. $^{13}$C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (11).

Figure S-25. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuS(C$_6$F$_5$)$_2$(CDP(Py)$_2$)] (9).
**Figure S-26.** $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuS(C$_6$F$_5$))$_2$(CDP(Py)$_2$)] (9).

(CDP(CH$_2$PPh$_2$)$_2$ (13))

**Figure S-27.** $^{31}$P NMR (Toluol, 101 MHz, [ppm]) of (CDP(CH$_2$PPh$_2$)$_2$ (13)).
**Figure S-28.** $^1$H NMR (C$_6$D$_6$, 300 MHz, [ppm]) of (CDP(CH$_2$PPh$_2$)$_2$ (13).

\[
[(\text{CuCl})_2(\text{CDP(CH}_2\text{PPh}_2)_2)] \quad \text{(14)}
\]

**Figure S-29.** $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [[CuCl]$_2$(CDP(CH$_2$PPh$_2$)$_2$] (14).
**Figure S-30.** $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuCl)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (14).

**Figure S-31.** $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuCl)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (14).
\[(\text{CuI})_2(\text{CDP(\text{CH}_2\text{PPh}_2)_2})\] (15)

Figure S-32. \(^{31}\text{P} \text{NMR (CCl}_2\text{D}_2, 101 \text{ MHz, [ppm]}}\) of \[(\text{CuI})_2(\text{CDP(\text{CH}_2\text{PPh}_2)_2})\] (15).

Figure S-33. \(^{31}\text{P} \text{NMR (CCl}_2\text{D}_2, 101 \text{ MHz, [ppm]}}\) of \[(\text{CuI})_2(\text{CDP(\text{CH}_2\text{PPh}_2)_2})\] (15).
Figure S-34. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuI)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (15).

$[(\text{CuSPh})_2(\text{CDP(CH}_2\text{PPh}_2)_2)]$ (16)

Figure S-35. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuSPh)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (16).
Figure S-36. \(^1\)H NMR (CCl\(_2\)D\(_2\), 300 MHz, [ppm]) of [(CuSPh)\(_2\)(CDP(CH\(_2\)PPh\(_2\))] (16).

\[\text{[CuCl(CDPH(CH\(_2\)PPh\(_2\))]PF}_6\text{ (17)}\]

Figure S-37. \(^{31}\)P NMR (CCl\(_2\)D\(_2\), 101 MHz, [ppm]) of [CuCl(CDPH(CH\(_2\)PPh\(_2\))]PF\(_6\) (17).
Figure S-38. $^{19}$F NMR (CCl$_2$D$_2$, 282 MHz, [ppm]) of [CuCl(CDPH(CH$_2$PPh)$_2$)]PF$_6$ (17).

$[\text{CuPPh}_3(\text{CH(PPh}_2\text{CHPPh}_2)_2)]$ (18)

Figure S-39. $^{31}$P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [CuPPh$_3$(CH(PPh$_2$CHPPh)$_2$)] (18).
Figure S-40. $^1$H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [CuPPh$_3$(CH(Ph$_2$CHPPh$_2$)$_2$] (18).
Figure S-41. Experimental IR Spectrum of [(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (4).
Crystallographic Data

\[(\text{CuCl})_2(\text{CDP(Py)})_2\] (2)

MKML27 | CCDC: 2017394

Crystal data

\[\text{C}_{35}\text{H}_{28}\text{Cl}_2\text{Cu}_2\text{N}_2\text{P}_2\] Block Yellow

Triclinic \(\overline{P}\) \(Z = 4\)

\[a = 10.5074(2) \text{ Å} \quad b = 15.9277(3) \text{ Å} \quad c = 19.8575(4) \text{ Å}\]

\[\alpha = 82.0400(10) \quad \beta = 80.765(2) \quad \gamma = 80.376(2) \quad \lambda = 1.54178 \text{ Å}\]

\[V = 3212.73(11) \text{ Å}^3 \quad \mu = 0.465 \text{ mm}^{-1} \quad F(000) = 1496 \]

\[0.182 \times 0.151 \times 0.094 \text{ mm}^3 \quad M = 0.73651 \text{ kg mol}^{-1} \quad D_{\text{calc}} = 1.523 \text{ g cm}^{-3}\]

\(N_{\text{ref}} = 43369\)

\(\Theta_{\text{min}} = 4.3^\circ\)

\(\Theta_{\text{max}} = 75.7^\circ\)

Data collection

X-Area Pilatus3\_SV 1.31.127.0 (Stoe, 2016)

\(\lambda = 1.54178 \text{ Å}\)

\(\Theta_{\text{min}} = 4.310^\circ\)

\(\Theta_{\text{max}} = 66.593^\circ\)

\(h = 12 \rightarrow -7\)

\(k = 18 \rightarrow -18\)

\(l = 23 \rightarrow -23\)

Structure solution / refinement

\(N_{\text{ref}} \text{ measured} = 43764\)

\(N_{\text{ref}} \text{ independent} = 11181\)

\(R_{\text{int}} = 0.0277\)

Semi-empirical from equivalents

\(T_{\text{max}} = 0.9848;\)

\(T_{\text{min}} = 0.4528\)

\(C_{25.00} = 98.6\%\)

\(N_{\text{ref}} \text{ used} = 11181\)

\(N_{\text{ref}} I > 2\sigma(I) = 9821\)

\(\Delta \rho_{\text{max}} = 0.507 \text{ eÅ}^{-3}\)

\(\Delta \rho_{\text{min}} = -0.614 \text{ eÅ}^{-3}\)

\(N_{\text{ref}} = 11181\)

\(N_{\text{restraints}} = 6\)

\(N_{\text{parameters}} = 795\)

\(R_{1}(I > 2\sigma(I)) = 0.0337\)

\(\omega R_{2}(I) = 0.0864\)

\(GooF(F^2) = 1.045\)
[(CuCl)_2(CDP(Py)_2)] (3)
MKP80 | CCDC: 2017392

Crystal data

C_{35}H_{28}I_{2}Cu_{2}N_{2}P_{2} Block Orange

Triclinic $P \overline{1}$ Z = 2

a = 12.0153(5) Å b = 12.8465(5) Å c = 13.5785(6) Å

$\alpha = 109.8360(10)$ ° $\beta = 94.1550(10)$ ° $\gamma = 93.9560(10)$ °

V = 1956.56(14) Å³ $\mu = 2.770$ mm⁻¹ $F(000) = 892$

0.140 x 0.130 x 0.110 mm³ $M = 0.91943$ kg·mol⁻¹ $D_{calc} = 1.561$ g·cm⁻³

$N_{ref} = 9708$ $\Theta_{min} = 2.5$ ° $\Theta_{max} = 26.6$ °

Data collection

D8 Quest (Bruker AXS Inc.) $T = 100(2)$ K $\lambda = 0.71073$ Å

$\Theta_{min} = 2.282$ ° $\Theta_{max} = 25.027$ °

$h = 14 \rightarrow -14$ $k = 15 \rightarrow -15$ $l = 16 \rightarrow -15$

Structure solution / refinement

$N_{ref}$ measured = 30066 $N_{ref}$ independent = 6918 $R_{int} = 0.0618$

Semi-empirical from equivalents $T_{max} = 0.7452$;

$T_{min} = 0.6292$ Full-matrix least-squares on $F^2$

$C_{25.00}^\ast = 99.9\%$ $N_{ref}$ used = 6918 $N_{ref} I>2\sigma(I) = 5356$

$\Delta \rho_{max} = 0.871$ eÅ⁻³ $\Delta \rho_{max} = -0.884$ eÅ⁻³

$N_{ref} = 6918$ $N_{restraints} = 36$ $N_{parameters} = 388$

$R_1(I>2\sigma(I)) = 0.0432$ $\omega R_2(I) = 0.0956$ $GooF(F^2) = 1.045$
[(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (4)

Crystal data

C$_{151}$H$_{129}$Cl$_{18}$Cu$_4$F$_{24}$N$_4$P$_{12}$

Block Yellow

Monoclinic

$Pn$

$Z = 2$

$a = 16.7727(6)$ Å

$b = 22.4945(8)$ Å

$c = 21.1551(7)$ Å

$\alpha = 90$ °

$\beta = 94.708(3)$ °

$\gamma = 90$ °

$V = 7954.8(5)$ Å$^3$

$\mu = 1.030$ mm$^{-1}$

$F(000) = 3762$

$M = 3.71953$ kg mol$^{-1}$

$D_\text{calc} = 1.553$ g cm$^{-3}$

$N_{\text{ref}} = 9066$

$\Theta_{\text{min}} = 2.3$ °

$\Theta_{\text{max}} = 27.8$ °

Data collection

D8 Quest (Bruker AXS Inc.)

$T = 100(2)$ K

$\lambda = 0.71073$ Å

$\Theta_{\text{min}} = 2.134$ °

$\Theta_{\text{max}} = 25.026$ °

$h = 19 \rightarrow -19$

$k = 24 \rightarrow -26$

$l = 25 \rightarrow -25$

Structure solution / refinement

$N_{\text{ref}}$ measured = 71983

$N_{\text{ref}}$ independent = 27071

$R_{\text{int}} = 0.0904$

$N_{\text{ref}}$ used = 27071

$N_{\text{ref}} I > 2\sigma(I) = 22422$

$N_{\text{ref}} I > 2\sigma(I) = 0.0609$

$\omega R_2(I) = 0.1560$

$GooF(F^2) = 1.035$
[(Cu(PPhOMe)₃)(CDP(Py)₂)][PF₆]₂ (5)
MKND122 | CCDC: 2017397

Crystal data

C₁₈₂H₁₉₆Cu₄F₂₄N₄O₁₉P₁₂ Block Yellow

Triclinic $P2_1/n$ $Z = 2$

$a = 18.8255(11)$ Å $b = 24.2698(15)$ Å $c = 20.5171(12)$ Å

$\alpha = 90^\circ$ $\beta = 110.359(2)^\circ$ $\gamma = 90^\circ$

$V = 8788.5(9)$ Å³ $\mu = 0.678$ mm⁻¹ $F(000) = 884.2$

$0.220 \times 0.181 \times 0.133$ mm³ $M = 3.82528$ kg·mol⁻¹ $D_{calc} = 1.446$ g·cm⁻³

$N_{ref} = 99844$ $\Theta_{min} = 2.3^\circ$ $\Theta_{max} = 28.8^\circ$

Data collection

D8 Quest (Bruker AXS Inc.) $T = 100(2)$ K $\lambda = 0.71073$ Å

$\Theta_{min} = 2.195^\circ$ $\Theta_{max} = 25.027^\circ$

$h = 22 \rightarrow -22$ $k = 28 \rightarrow -28$ $l = 24 \rightarrow -24$

Structure solution / refinement

$N_{ref}$ measured = 123356 $N_{ref}$ independent = 15519 $R_{int} = 0.0738$

Semi-empirical from equivalents $T_{max} = 0.7458$; $T_{min} = 0.6659$ Full-matrix least-squares on $F^2$

$C_{25.00}^\circ = 99.4\%$ $N_{ref}$ used = 15519 $N_{ref} I > 2\sigma(I) = 12059$

$\Delta \rho_{max} = 1.121$ eÅ⁻³ $\Delta \rho_{max} = -0.753$ eÅ⁻³

$N_{ref} = 15519$ $N_{restraints} = 55$ $N_{parameters} = 1176$

$R_1(I > 2\sigma(I)) = 0.0449$ $\omega R_2(I) = 0.1170$ $GooF(F^2) = 1.023$
Crystal data

\( \text{C}_{73}\text{H}_{60}\text{Cl}_{4}\text{Cu}_{2}\text{F}_{12}\text{N}_{2}\text{OP}_{6} \)  Block  Intense Yellow

Triclinic  \( P\overline{1} \)  \( Z = 2 \)

\( a = 13.2598(8) \) Å  \( b = 13.7699(8) \) Å  \( c = 23.8017(15) \) Å

\( \alpha = 87.929(2) \) °  \( \beta = 78.411(2) \) °  \( \gamma = 68.542(2) \) °

\( V = 3958.9(4) \) Å\(^3\)  \( \mu = 0.864 \) mm\(^{-1}\)  \( F(000) = 1688 \)

\( 0.520 \times 0.216 \times 0.199 \) mm\(^3\)  \( M = 1.66395 \) kg\(\cdot\)mol\(^{-1}\)  \( D_{\text{calc}} = 1.396 \) g\(\cdot\)cm\(^{-3}\)

\( N_{\text{ref}} = 9851 \)  \( \Theta_{\text{min}} = 2.6 \) °  \( \Theta_{\text{max}} = 29.1 \) °

Data collection

D8 Quest (Bruker AXS Inc.)  \( T = 100(2) \) K  \( \lambda = 0.71073 \) Å

\( \Theta_{\text{min}} = 2.156 \) °  \( \Theta_{\text{max}} = 25.027 \) °

\( h = 15 \rightarrow -15 \)  \( k = 16 \rightarrow -16 \)  \( l = 28 \rightarrow -28 \)

Structure solution / refinement

\( N_{\text{ref measured}} = 81101 \)  \( N_{\text{ref independent}} = 13988 \)  \( R_{\text{int}} = 0.0466 \)

Semi-empirical from equivalents  \( T_{\text{max}} = 0.7458 \)  Full-matrix least-squares on \( F^2 \)

\( T_{\text{min}} = 0.6532 \)

\( C_{25.00} = 99.9\% \)  \( N_{\text{ref used}} = 13988 \)

\( \Delta \rho_{\text{max}} = 0.525 \) e\(\cdot\)Å\(^{-3}\)  \( \Delta \rho_{\text{max}} = -0.708 \) e\(\cdot\)Å\(^{-3}\)

\( N_{\text{ref}} = 13988 \)  \( N_{\text{restraints}} = 24 \)  \( N_{\text{parameters}} = 908 \)

\( R_1(I>2\sigma(I)) = 0.0510 \)  \( \omega R_2(I) = 0.1166 \)  \( GooF(F^2) = 1.076 \)
Crystal data

\[ \text{C}_{76}\text{H}_{64}\text{Cl}_{4}\text{Cu}_{2}\text{F}_{12}\text{N}_{2}\text{OP}_{6} \] Block Fluorescent Yellow

Triclinic \( P\overline{1} \)

\( a = 12.7458(6) \) \( \text{Å} \) \( b = 13.1266(6) \) \( \text{Å} \) \( c = 21.8612(11) \) \( \text{Å} \)
\( \alpha = 87.898(2) \) \( ^{\circ} \) \( \beta = 83.248(2) \) \( ^{\circ} \) \( \gamma = 83.122(2) \) \( ^{\circ} \)

\( V = 3605.1(3) \) \( \text{Å}^3 \) \( \mu = 0.951 \) \( \text{mm}^{-1} \) \( F(000) = 1732 \)

\( 0.324 \times 0.267 \times 0.172 \) \( \text{mm}^3 \) \( M = 1.70402 \) \( \text{kg} \cdot \text{mol}^{-1} \) \( D_{\text{calc}} = 1.570 \) \( \text{g} \cdot \text{cm}^{-3} \)

\( N_{\text{ref}} = 9459 \) \( \Theta_{\text{min}} = 2.3 \) \( ^{\circ} \) \( \Theta_{\text{max}} = 29.2 \) \( ^{\circ} \)

Data collection

D8 Quest (Bruker AXS Inc.) \( T = 100(2) \) \( \text{K} \) \( \lambda = 0.71073 \) \( \text{Å} \)

\( \Theta_{\text{min}} = 2.116 \) \( ^{\circ} \) \( \Theta_{\text{max}} = 25.027 \) \( ^{\circ} \)

\( h = 15 \rightarrow -15 \) \( k = 15 \rightarrow -15 \) \( l = 26 \rightarrow -26 \)

Structure solution / refinement

\( N_{\text{ref}} \) measured = 80679 \( N_{\text{ref}} \) independent = 12680 \( R_{\text{int}} = 0.0270 \)

Semi-empirical from equivalents \( T_{\text{max}} = 0.7458; \) \( T_{\text{min}} = 0.6926 \) \( R_{\text{max}} = 99.6\% \)

\( C_{25.00}^{+} = 99.6\% \) \( N_{\text{ref}} \) used = 12680 \( N_{\text{ref}} I > 2 \sigma(I) = 11570 \)

\( \Delta \rho_{\text{max}} = 0.735 \) \( \text{eÅ}^{-3} \) \( \Delta \rho_{\text{max}} = -0.496 \) \( \text{eÅ}^{-3} \)

\( N_{\text{ref}} = 12680 \) \( N_{\text{restraints}} = 0 \) \( N_{\text{parameters}} = 930 \)

\( R(I > 2 \sigma(I)) = 0.0276 \) \( wR_{2}(I) = 0.0718 \) \( GooF(F^2) = 1.023 \)
Crystal data

C$_{72}$H$_{62}$Cl$_6$Cu$_2$FeN$_2$P$_6$  Block  Yellow

Triclinic  $P\bar{1}$  $Z = 2$

a = 13.1967(3) Å  b = 13.7697(3) Å  c = 22.6159(5) Å

$\alpha = 85.242(2)$ °  $\beta = 81.225(2)$ °  $\gamma = 67.120(2)$ °

V = 3740.72(15) Å$^3$  $\mu = 6.015$ mm$^{-1}$  $F(000) = 1784$

0.135 x 0.090 x 0.046 mm$^3$  $M = 1.76471$ kg·mol$^{-1}$  $D_{\text{calc}} = 1.567$ g·cm$^{-3}$

$N_{\text{ref}} = 27362$  $\Theta_{\text{min}} = 3.7$ °  $\Theta_{\text{max}} = 75.6$ °

Data collection

X-Area Pilatus3_SV 1.31.127.0 (Stoe, 2016)  $\lambda = 1.54178$ Å

$\Theta_{\text{min}} = 3.667$ °  $\Theta_{\text{max}} = 66.595$ °  $T = 100(2)$ K

$h = 15 \rightarrow -14$  $k = 16 \rightarrow -14$  $l = 26 \rightarrow -23$

Structure solution / refinement

$N_{\text{ref}}$ measured = 65269  $N_{\text{ref}}$ independent = 13098  $R_{\text{int}} = 0.0734$

Semi-empirical from equivalents  $T_{\text{max}} = 0.9498$;  $T_{\text{min}} = 0.2242$

$C_{25.00} = 99.0\%$  $N_{\text{ref}}$ used = 13098  $N_{\text{ref}}$ $I > 2\sigma(I) = 8522$

$\Delta \rho_{\text{max}} = 3.149$ eÅ$^{-3}$  $\Delta \rho_{\text{max}} = -1.060$ eÅ$^{-3}$

$N_{\text{ref}} = 13098$  $N_{\text{restraints}} = 100$  $N_{\text{parameters}} = 1098$

$R_1(I > 2\sigma(I)) = 0.1041$  $\omega R_2(I) = 0.3047$  $GooF(F^2) = 1.120$
[(CuCarb)$_2$(CDP(Py)$_2$)] (11)

MKML23b | CCDC: 2017393

Crystal data

C$_{61}$H$_{48}$Cl$_4$Cu$_2$N$_4$P$_2$

Block

Yellow

Monoclinic $P2_1/n$

Z = 4

a = 12.9899(2) Å

b = 26.8839(4) Å

c = 16.5110(2) Å

$\alpha$ = 90°

$\beta$ = 111.9520(10)°

$\gamma$ = 90°

V = 5347.91(14) Å$^3$

$\mu$ = 3.730 mm$^{-1}$

F(000) = 2392

0.183 x 0.127 x 0.072 mm$^3$

$M$ = 1.16787 kg·mol$^{-1}$

$D_{calc}$ = 1.450 g·cm$^{-3}$

$N_{ref}$ = 48688

$\Theta_{min}$ = 3.3°

$\Theta_{max}$ = 76.1°

Data collection

X-Area Pilatus3_SV 1.31.127.0 (Stoe, 2016)

$\lambda$ = 1.54178 Å

$\Theta_{min}$ = 3.725°

$\Theta_{max}$ = 66.590°

h = 15 → −15

k = 32 → −19

l = 19 → −19

Structure solution / refinement

$N_{ref}$ measured = 51910

$N_{ref}$ independent = 9382

$R_{int}$ = 0.0306

Semi-empirical from equivalents

$T_{max}$ = 0.9848;

$T_{min}$ = 0.4696

Full-matrix least-squares on $F^2$

$C_{25.00}$ = 99.3%

$N_{ref}$ used = 9382

$N_{ref}$ I$>2\sigma(I)$ = 8139

$\Delta \rho_{max}$ = 1.069 eÅ$^{-3}$

$\Delta \rho_{max}$ = −1.097 eÅ$^{-3}$

$N_{ref}$ = 9382

$N_{restraints}$ = 22

$N_{parameters}$ = 680

$R_1(I>2\sigma(I))$ = 0.0445

$\omega R_2(I)$ = 0.1200

$GooF(F^2)$ = 1.031
[(CuS(C₆F₅))₂(CDP(Py)₂)] (9)
MKMN26 | CCDC: 2017395

**Crystal data**

C₄₇H₂₈Cu₂F₁₀N₂P₂S₂ Needle Orange

Triclinic $P\overline{1}$

$\bar{a} = 10.295(2) \ \text{Å}$

$\bar{b} = 13.312(3) \ \text{Å}$

$\bar{c} = 16.579(3) \ \text{Å}$

$\alpha = 71.143(5) \ ^\circ$

$\beta = 85.319(6) \ ^\circ$

$\gamma = 80.351(6) \ ^\circ$

$V = 2118.8(8) \ \text{Å}^3$

$\mu = 1.261 \ \text{mm}^{-1}$

$0.358 \times 0.117 \times 0.056 \ \text{mm}^3$

$M = 1.06385 \ \text{kg} \cdot \text{mol}^{-1}$

$D_{\text{calc}} = 1.667 \ \text{g} \cdot \text{cm}^{-3}$

$N_{\text{ref}} = 9758$

$\Theta_{\text{min}} = 2.4^\circ$

$\Theta_{\text{max}} = 28.5^\circ$

**Data collection**

D8 Quest (Bruker AXS Inc.) $T = 100(2) \ \text{K}$

$\lambda = 0.71073 \ \text{Å}$

$\Theta_{\text{min}} = 2.359^\circ$

$\Theta_{\text{max}} = 29.161^\circ$

$h = 14 \rightarrow -14$

$k = 18 \rightarrow -18$

$l = 22 \rightarrow -20$

**Structure solution / refinement**

$N_{\text{ref}}$ measured = 69728

$N_{\text{ref}}$ independent = 11371

$R_{\text{int}} = 0.0698$

Semi-empirical from equivalents

$T_{\text{max}} = 0.7458$;

$T_{\text{min}} = 0.6599$

$C_{25.00} = 99.9\%$

$N_{\text{ref}}$ used = 11371

$N_{\text{ref}}$ $I > 2\sigma(I) = 7885$

$N_{\text{ref}} I > 2\sigma(I) = 0.0527$

$N_{\text{parameters}} = 586$

$\Delta \rho_{\text{max}} = 2.804 \ \text{eÅ}^{-3}$

$\Delta \rho_{\text{max}} = -1.643 \ \text{eÅ}^{-3}$

$R_1(I > 2\sigma(I)) = 0.0527$

$\omega R_2(I) = 0.1115$

$GooF(F^2) = 1.028$
Crystal data

Cs5H52Cl10Cu2P4  Block  Clear Colourless
Triclinic  p̅1  Z = 2
a = 12.0702(8) Å  b = 12.8612(9) Å  c = 20.0342(13) Å
α = 84.966(2) °  β = 75.555(2) °  γ = 73.976(2) °
V = 2894.1(3) Å³  μ = 1.344 mm⁻¹  F(000) = 1340
0.560 x 0.390 x 0.240 mm³  M = 1.31845 kg·mol⁻¹  Dcalc = 1.513 g·cm⁻³
Nref = 9305  Θmin = 2.4 °  Θmax = 29.2 °

Data collection

D8 Quest (Bruker AXS Inc.)  T = 100(2) K  λ = 0.71073 Å
Θmin = 2.293 °  Θmax = 25.027 °
h = 14 → −14  k = 15 → −15  l = 23 → −23

Structure solution / refinement

Nref measured = 64909  Nref independent = 10222  Rint = 0.0377
Semi-empirical from equivalents  Tmax = 0.7458;  Full-matrix least-squares on F²
Tmin = 0.6081
C25.00 % = 99.9%  Nref used = 10222  Nref I>2σ(I) = 8783
Δρmax = 0.439 eÅ⁻³  Δρmax = −0.635 eÅ⁻³
Nref = 10222  Nrestraints = 6  Nparameters = 695
R1(I>2σ(I)) = 0.0314  ωR2(I) = 0.0736  GooF(F²) = 1.056
Crystal data

C_{51}H_{44}Cu_{2}I_{2}P_{4}  

Block  

Translucent Yellow

Monoclinic  

\( C2/c \)  

\( Z = 4 \)

\( a = 15.1057(8) \) Å  

\( b = 17.1264(9) \) Å  

\( c = 20.0035(11) \) Å

\( \alpha = 90^\circ \)  

\( \beta = 93.099(2) ^\circ \)  

\( \gamma = 90^\circ \)

\( V = 5167.5(5) \) Å\(^3\)  

\( \mu = 2.173 \) mm\(^{-1}\)  

\( F(000) = 2296 \)

\( 0.440 \times 0.286 \times 0.231 \) mm\(^3\)  

\( M = 1.16162 \) kg\( \cdot \)mol\(^{-1}\)  

\( D_{\text{calc}} = 1.4923 \) g\( \cdot \)cm\(^{-3}\)

\( N_{\text{ref}} = 9712 \)  

\( \Theta_{\text{min}} = 2.4^\circ \)  

\( \Theta_{\text{max}} = 28.5^\circ \)

Data collection

D8 Quest (Bruker AXS Inc.)  

\( T = 100(2) \) K

\( \lambda = 0.71073 \) Å  

\( \Theta_{\text{min}} = 2.104^\circ \)  

\( \Theta_{\text{max}} = 29.272^\circ \)

\( h = 20 \rightarrow -19 \)  

\( k = 23 \rightarrow -23 \)  

\( l = 26 \rightarrow -26 \)

Structure solution / refinement

\( N_{\text{ref}} \) measured = 82870  

\( N_{\text{ref}} \) independent = 6967  

\( R_{\text{int}} = 0.0740 \)

\( N_{\text{ref}} \) used = 6967  

\( N_{\text{ref}} I > 2\sigma(I) = 5325 \)

\( N_{\text{ref}} \) measured  

\( N_{\text{ref}} \) independent  

\( N_{\text{ref}} \) used  

\( N_{\text{ref}} I > 2\sigma(I) \)

\( \Delta \rho_{\text{max}} = 2.286 \) eÅ\(^{-3}\)  

\( \Delta \rho_{\text{max}} = -2.211 \) eÅ\(^{-3}\)

\( N_{\text{ref}} = 6967 \)  

\( N_{\text{restraints}} = 12 \)  

\( N_{\text{parameters}} = 268 \)

\( R_1(I > 2\sigma(I)) = 0.0603 \)  

\( \omega R_2(I) = 0.1889 \)  

\( GooF(F^2) = 1.043 \)
[(CuSPh)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (16)
MKP199 | CCDC: 2017409

Crystal data

C$_{138}$H$_{132}$Cu$_4$O$_3$P$_8$S$_4$

Needle

Fluorescent Yellow

Triclinic $Par{1}$

$Z = 2$

$\alpha = 63.399(3) ^\circ$

$c = 20.393(2) \ \text{Å}$

$\beta = 84.454(3) ^\circ$

$\gamma = 86.908(3) ^\circ$

$V = 5996.6(11) \ \text{Å}^3$

$F(000) = 2568$

$\mu = 0.930 \ \text{mm}^{-1}$

$M = 2.46864 \ \text{kg} \cdot \text{mol}^{-1}$

$D_{\text{calc}} = 1.367 \ \text{g} \cdot \text{cm}^{-3}$

$\Theta_{\text{min}} = 2.2 ^\circ$

$\Theta_{\text{max}} = 23.9 ^\circ$

Data collection

D8 Quest (Bruker AXS Inc.)

$T = 100(2) \ \text{K}$

$\lambda = 0.71073 \ \text{Å}$

$\Theta_{\text{min}} = 2.241 ^\circ$

$\Theta_{\text{max}} = 25.027 ^\circ$

$h = 19 \rightarrow -19$

$k = 21 \rightarrow -24$

$l = 24 \rightarrow 0$

Structure solution / refinement

$N_{\text{ref measured}} = 21786$

$N_{\text{ref independent}} = 21786$

$R_{\text{int}} = 0.00$

$N_{\text{ref used}} = 21786$

$N_{\text{ref I}>2\sigma(I)} = 12003$

$\Delta \rho_{\text{max}} = 0.994 \ \text{eÅ}^{-3}$

$\Delta \rho_{\text{max}} = -0.940 \ \text{eÅ}^{-3}$

$N_{\text{ref}} = 21786$

$N_{\text{restraints}} = 2036$

$N_{\text{parameters}} = 1415$

$R_1(I)>2\sigma(I)) = 0.1125$

$\omega R_2(I) = 0.1874$

$\text{GooF}(F^2) = 1.050$
[CuCl(CDP(CH_2PPh_2)_2]PF_6 (17)
MKP42 | CCDC: 2017407

**Crystal data**

C_{52}H_{47}Cl_3CuF_6P_5  
Block  
Cleat Colourless

Monoclinic  
C2/c  
Z = 2

a = 23.7049(12) Å  
b = 11.6976(6) Å  
c = 38.147(2) Å

α = 90 °  
β = 105.731(2) °  
γ = 90 °

V = 10181.5(10) Å³  
μ = 0.801 mm⁻¹  
F(000) = 4544

0.440 x 0.221 x 0.186 mm³  
M = 1.449 kg·mol⁻¹  
D_{calc} = 1.449 g·cm⁻³

N_{ref} = 9113  
Θ_{min} = 2.2 °  
Θ_{max} = 27.1 °

**Data collection**

D8 Quest (Bruker AXS Inc.)  
T = 100(2) K  
λ = 0.71073 Å

Θ_{min} = 2.219 °  
Θ_{max} = 25.024 °

h = 28 → –28  
k = 13 → –13  
l = 45 → –45

**Structure solution / refinement**

N_{ref} measured = 114090  
N_{ref} independent = 8988  
R_{int} = 0.0449

Semi-empirical from equivalents  
T_{max} = 0.7455;  
T_{min} = 0.7042  
Full-matrix least-squares on F²

C_{25.00}^+ = 99.9%  
N_{ref} used = 8988  
N_{ref} I>2σ(I) = 7804

Δρ_{max} = 0.748 eÅ⁻³  
Δρ_{max} = –0.941 eÅ⁻³

N_{ref} = 8988  
N_{restraints} = 0  
N_{parameters} = 625

R_I(I>2σ(I)) = 0.0332  
ωR_2(I) = 0.0755  
GooF(F²) = 1.050
[CuPPh₃(CH(PPh₂CHPPh₂)₂)] (18)
MKPCR28 | CCDC: 2017411

Crystal data

C₇₃H₆₆CuOP₅  Block  Yellow  Z = 4

Monoclinic  P2₁/c

a = 15.5803(8) Å  b = 15.8868(8) Å  c = 24.0979(11) Å

α = 90 °  β = 94.733(2) °  γ = 90 °

V = 5944.4(5) Å³  μ = 0.548 mm⁻¹  F(000) = 2464

0.440 x 0.221 x 0.186 mm³  M = 1.17764 kg·mol⁻¹  Dcalc = 1.492 g·cm⁻³

Nref = 9982  Θmin = 2.4 °  Θmax = 28.7 °

Data collection

D8 Quest (Bruker AXS Inc.)  T = 100(2) K  λ = 0.71073 Å

Θmin = 2.065 °  Θmax = 25.025 °

h = 18 → −18  k = 18 → −18  l = 28 → −28

Structure solution / refinement

Nref measured = 104671  Nref independent = 10497  Rtot = 0.0679

Semi-empirical from equivalents  Tmax = 0.7458;  Tmin = 0.6758

C25.00 = 99.9%  Nref used = 10497  Nref I>2σ(I) = 8931

Δρmax = 0.838 eÅ⁻³  Δρmax = −0.424 eÅ⁻³

Nref = 10497  Nrestraints = 0  Nparameters = 721

R1(I>2σ(I)) = 0.0471  wR2(I) = 0.1098  GooF(F²) = 1.164
Chemical calculations

Density functional theory (DFT) using the PBE\textsuperscript{8,9} functional was performed to complex 8 and 10. The def2-TZVPP\textsuperscript{10–12} basis set was used, employing the resolution-of-identity approximation.\textsuperscript{13–16} Further, D3-dispersion correction\textsuperscript{17} was considered applying the BECKE-JOHNSON damping.\textsuperscript{18–21} To verify that ground state and excited states are minima on the potential energy surface, analytical harmonic vibrational frequency calculations were conducted. Structural optimizations, TD-DFT and SOC-TD-DFT calculations were performed using ORCA 3.0.3.\textsuperscript{22}

Deprotonation of 19

Table 1 Atomic partial charges $q$(C) of 19 calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q$(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.10401</td>
</tr>
<tr>
<td>C2</td>
<td>-1.09837</td>
</tr>
<tr>
<td>C3</td>
<td>-1.09833</td>
</tr>
<tr>
<td>P1</td>
<td>1.67805</td>
</tr>
<tr>
<td>P2</td>
<td>1.67807</td>
</tr>
<tr>
<td>P3</td>
<td>0.83356</td>
</tr>
<tr>
<td>P4</td>
<td>0.83358</td>
</tr>
<tr>
<td>Sum</td>
<td>1.72255</td>
</tr>
</tbody>
</table>

Table 2 Atomic partial charges $q$(C) of 19a calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q$(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.39295</td>
</tr>
<tr>
<td>C2</td>
<td>-1.08756</td>
</tr>
<tr>
<td>C3</td>
<td>-1.08921</td>
</tr>
<tr>
<td>P1</td>
<td>1.67469</td>
</tr>
<tr>
<td>P2</td>
<td>1.66442</td>
</tr>
<tr>
<td></td>
<td>Partial Charge (q)</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------</td>
</tr>
<tr>
<td>P3</td>
<td>0.82549</td>
</tr>
<tr>
<td>P4</td>
<td>0.82719</td>
</tr>
<tr>
<td>Sum</td>
<td>1.42207</td>
</tr>
</tbody>
</table>

Table 3: Atomic partial charges $q(C)$ of **12b** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>Partial Charge (q)</th>
</tr>
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<tbody>
<tr>
<td>C1</td>
<td>-1.10903</td>
</tr>
<tr>
<td>C2</td>
<td>-1.11819</td>
</tr>
<tr>
<td>C3</td>
<td>-1.34607</td>
</tr>
<tr>
<td>P1</td>
<td>1.69060</td>
</tr>
<tr>
<td>P2</td>
<td>1.66433</td>
</tr>
<tr>
<td>P3</td>
<td>0.82873</td>
</tr>
<tr>
<td>P4</td>
<td>0.82147</td>
</tr>
<tr>
<td>Sum</td>
<td>1.43184</td>
</tr>
</tbody>
</table>

Table 4: Atomic partial charges $q(C)$ of **13a** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.
Table 5  Atomic partial charges $q(C)$ of 13b calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q(C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.07747</td>
</tr>
<tr>
<td>C2</td>
<td>-1.34641</td>
</tr>
<tr>
<td>C3</td>
<td>-1.34810</td>
</tr>
<tr>
<td>P1</td>
<td>1.66134</td>
</tr>
<tr>
<td>P2</td>
<td>1.66292</td>
</tr>
<tr>
<td>P3</td>
<td>0.82119</td>
</tr>
<tr>
<td>P4</td>
<td>0.82274</td>
</tr>
<tr>
<td>Sum</td>
<td>1.19621</td>
</tr>
</tbody>
</table>

Table 6  Atomic partial charges $q(C)$ of 13c calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q(C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.45006</td>
</tr>
<tr>
<td>C2</td>
<td>-1.09378</td>
</tr>
<tr>
<td>C3</td>
<td>-1.09380</td>
</tr>
<tr>
<td>P1</td>
<td>1.61564</td>
</tr>
<tr>
<td>P2</td>
<td>1.61565</td>
</tr>
<tr>
<td>P3</td>
<td>0.81602</td>
</tr>
<tr>
<td>P4</td>
<td>0.81602</td>
</tr>
<tr>
<td>Sum</td>
<td>1.22569</td>
</tr>
</tbody>
</table>
Table 7 Atomic partial charges $q(C)$ of 13d calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

| C1  | -1.04315 |
| C2  | -1.06590 |
| C3  | -1.38125 |
| P1  | 1.58938  |
| P2  | 1.58578  |
| P3  | 0.82062  |
| P4  | 0.79698  |
| Sum | 1.30246  |

Table 8 Atomic partial charges $q(C)$ of 20a calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

| C1  | -1.38576 |
| C2  | -1.37257 |
| C3  | -1.37253 |
| P1  | 1.67775  |
| P2  | 1.67769  |
| P3  | 0.83322  |
| P4  | 0.83321  |
| Sum | 0.89101  |
Table 8 Atomic partial charges $q(C)$ of 20b calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q(C)$</th>
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</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.49850</td>
</tr>
<tr>
<td>C2</td>
<td>-1.11141</td>
</tr>
<tr>
<td>C3</td>
<td>-1.36223</td>
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<tr>
<td>P1</td>
<td>1.59666</td>
</tr>
<tr>
<td>P2</td>
<td>1.64607</td>
</tr>
<tr>
<td>P3</td>
<td>0.82008</td>
</tr>
<tr>
<td>P4</td>
<td>0.82936</td>
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<tr>
<td>Sum</td>
<td>0.92003</td>
</tr>
</tbody>
</table>

Table 8 Atomic partial charges $q(C)$ of 20c calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.

<table>
<thead>
<tr>
<th></th>
<th>$q(C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-1.31933</td>
</tr>
<tr>
<td>C2</td>
<td>-1.06983</td>
</tr>
<tr>
<td>C3</td>
<td>-1.41583</td>
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<tr>
<td>P1</td>
<td>1.58006</td>
</tr>
<tr>
<td>P2</td>
<td>1.60939</td>
</tr>
<tr>
<td>P3</td>
<td>0.83700</td>
</tr>
<tr>
<td>P4</td>
<td>0.84920</td>
</tr>
<tr>
<td>Sum</td>
<td>1.07066</td>
</tr>
</tbody>
</table>
Scheme S-1. Calculation of the stepwise deprotonation of \([\text{CH}_2(\text{PPh}_2\text{CPPh}_2)_2]\text{Cl}_2\) (19). Stable tautomers are shown with their corresponding energy difference in kcal/mol. The positive value of the energy corresponds to the energy that has to be applied in order to convert one molecule into the other. The most stable tautomer is shown on the left side.
Figure S-42. Kohn-Sham orbitals of HOMO-1, HOMO, LUMO and LUMO+1 for [(CuCl)$_2$(CDP(CH$_2$PPh$_2$)$_2$)]$_2$ (14) calculated for the optimized gas phase $S_0$ state geometry (isovalue = 0.05). Calculations were performed at the PBE-D3(BJ)/def2-TZVPP level of theory.
Figure S-43. Kohn-Sham orbitals of HOMO-1, HOMO, LUMO and LUMO+1 for [(CuSPh)_2(CDP(CH_2PPh_2)_2)] (16) calculated for the optimized gas phase S_0 state geometry (isovalue = 0.05). Calculations were performed at the PBE-D3(BJ)/def2-TZVPP level of theory.

Atomic coordinates

For Atomic coordinates see the XYZ file.

Literature


