Supporting Information

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

Marius Klein[a], *Nemrud Demirel*, *Alexander Schinabeck*[b], *Hartmut Yersin*[b], *Jörg Sundermeyer**[a]

[a] Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35043 Marburg, Germany
[b] Institute for Physical Chemistry, University of Regensburg, 93040 Regensburg, Germany

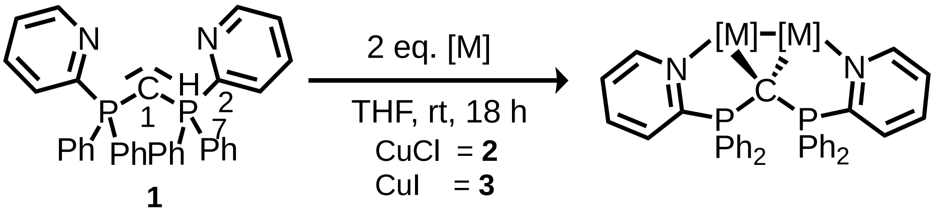
Table of Contents

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)$_2$[2] and (CH$_2$)(dppm)$_2$[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 δ 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-FT-IR 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 (diameterd=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



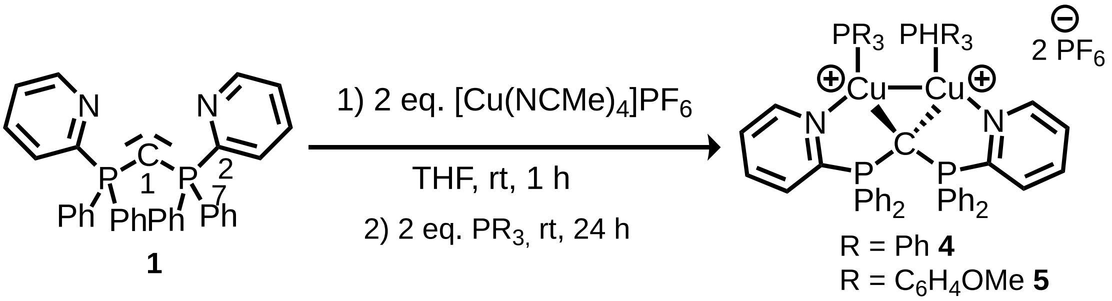
[(CuCl)$_2$(CDP(Py)$_2$)] (2)

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): δ 21.4 (s) ppm. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz): δ 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): δ

155.0-153.8 (m, *C*2), 149.9 (t, $^{3}J_{C,P}$ = 8.12 Hz, *C*6), 137.9 (t, ^{3}JC,P = 5.03 Hz, *C*4), 133.4 (t, $^{2}J_{C,P}$ = 4.97 Hz, *C*8), 132.6 (s, *C*10), 129.1 (t, $^{3}J_{C,P}$ = 5.82 Hz, *C*9), 128.8-127.8 (m, *C*7), 128.0 (m, *C*3), 126.8 (s, *C*5), -3.9 (m, *C*1) ppm. APCI-MS: *m/z* 735.1 $[M+H]^{+}$. Elem. anal. (%) found C, 56.49; H, 3.92; N, 4.05; $C_{35}H_{28}N_{2}P_{2}Cu_{2}Cl_{2}$ required C, 57.07; H, 3.83; N, 3.80.

$[(CuI)_{2}(CDP(Py)_{2})]$ (3)

A 100 mg portion (0.19 mmol, 1 eq.) of **1** and 71 mg (0.37 mmol, 2 eq.) of cupper(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): δ 21.5 (s) ppm. ^{1}H NMR ($CCl_{2}D_{2}$, 300 MHz): δ 8.98-8.97 (d, $J_{H,H}$ = 4.9 Hz, 2H, *H*6), 7.79-7.75 (m, 2H, *H*4), 7.65-7.59 (m, 10H, *H*8, *H*5), 7.44 (tt, $J_{H,H}$ =0.8, 7.5 Hz, 4H, *H*10), 7.39-7.36 (m, 2H, *H*3), 7.26-7.3 (m, 8H, *H*9) ppm. ^{13}C NMR ($CCl_{2}D$, 75 MHz): δ 150.9 (m, *C*6), 137.9 (t, ^{3}JC,P = 5.5 Hz, *C*4), 133.6 (t, $^{2}J_{C,P}$ = 4.9 Hz, *C*8), 132.7 (s, *C*10), 129.3 (t, $^{3}J_{C,P}$ = 5.7 Hz, *C*9), 128.7 (m, *C*7), 128.3 (s, *C*3), 127.2 (s, *C*5) ppm. Elem. anal. (%) found C, 45.52; H, 3.32; N, 3.25; $C_{35}H_{28}N_{2}P_{2}Cu_{2}Cl_{2}$ required C, 45.72; H, 3.07; N, 3.05.

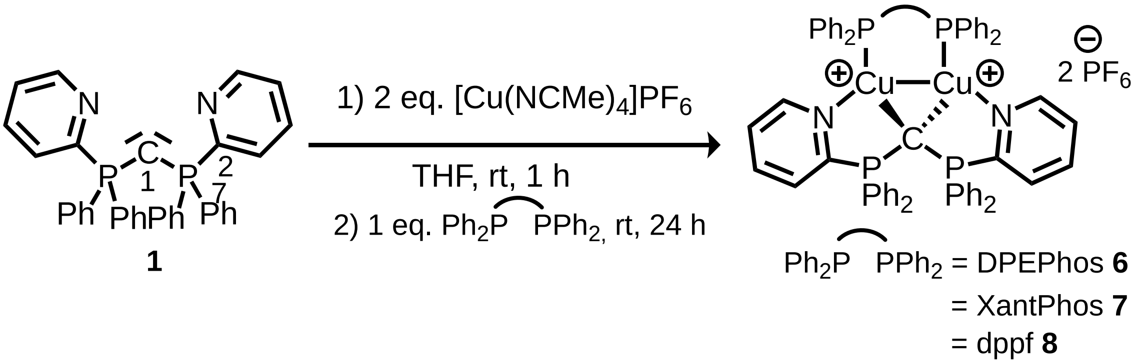


$[(CuPPh_{3})_{2}(CDP(Py)_{2})](PF_{6})_{2}$ (4)

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 (0.18 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): δ 32.9 (s), 3.5 (s), 145.1 (sep.) ppm. ^{1}H NMR ($CCl_{2}D_{2}$, 300 MHz): δ 8.13 (t, $J_{H,H}$ = 7.5 Hz, 2H, CH_{arom}), 7.96 (d, $J_{H,H}$ =4.8 Hz, 2H, CH_{arom}), 7.71-7.68 (m, 2H, CH_{arom}), 7.57 (t, $J_{H,H}$ = 6.0 Hz, 2H, CH_{arom}), 7.47 (q, $J_{H,H}$ = 8.4 Hz, 10H, CH_{arom}), 7.28-7.15 (m, 20H, CH_{arom}), 7.07 (t, $J_{H,H}$ =7.2 Hz, 8H, CH_{arom}), 6.93 (dd, $J_{H,H}$ =7.4, 11.3 Hz, 12H, CH_{arom}) ppm. ^{13}C NMR ($CCl_{2}D$, 75 MHz): δ 151.3, 146.2, 141.0, 134.3, 133.9, 133.7, 133.2 (t, $^{2}J_{C,P}$ = 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. ϕ_{PL} = 36%.

$[(Cu(PC_6H_4OMe)_3)_2(CDP(Py)_2)](PF_6)_2$ (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 $2 \cdot 5$ ml of diethyl ether and $2 \cdot 5$ ml of pentane. The light yellow residue was dried in vacuo and collected in a 47% yield (72.0 mg, 0.04 mmol). $^{31}P\{H\}$ NMR (CCl_2D_2, 101 MHz): δ 32.8 (s), –0.3 (s), 144.5 (sep.) ppm. ^1H NMR (CCl_2D_2, 300 MHz): δ 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, $6 \cdot CH_3$) ppm. ^{13}C NMR (CCl_2D, 75 MHz): δ 162.6, 151.4, 140.7, 135.3 (d, $^2J_{C,P}$ = 16.1 Hz), 134.2, 133.3 (t, $^2J_{C,P}$ = 4.9 Hz), 130.1 (t, $^2J_{C,P}$ = 6.0 Hz), 129.2, 122.4, 121.8, 115.6 (d, $^2J_{C,P}$ = 11.2 Hz), 56.1 ppm. Elem. anal. (%) found C, 57.98; H, 4.29; N, 1.89; $C_{77}H_{70}N_2P_6O_6Cu_2F_{12}$ required C, 57.07; H, 3.78; N, 1.87.



$[Cu_2(DPEPhos)(CDP(Py)_2)](PF_6)_2$ (6)

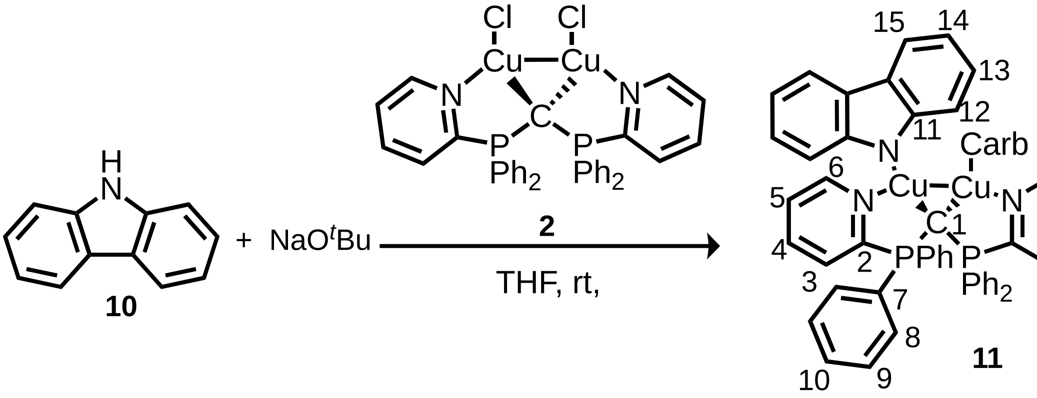
A 50.0 mg portion (0.09 mmol, 1 eq.) of **1** and 69.2 mg (0.18 mmol, 2 eq.) of tetrakis(acetonitrile)copper(I) hexafluorophosphate were treated with 5.0 ml THF at room temperature and stirred for 1 h. A change in colour was observed (red→dark red→brown→orange→clear yellow). A 50.0 mg portion (0.09 mmol, 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 $2 \cdot 5$ ml of diethyl ether and $2 \cdot 5$ 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_2D_2, 101 MHz): δ 29.7 (s), –8.7 (s), 144.5 (sep.) ppm. ^1H NMR (CCl_2D_2, 300 MHz): δ 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; $C_{71}H_{56}N_2P_6Cu_2F_{12}O$ 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 $2 \cdot 5$ ml of diethyl ether and $2 \cdot 5$ 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_2D_2, 101 MHz): δ 34.9 (s), –6.1 (s), 143.8 (sep.) ppm. ^{1}H NMR (CCl_2D_2, 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, $2 \cdot CH_3$). ^{13}C NMR (CCl_2D, 75 MHz): δ 156.2, 155.5, 151.6 (d, $^2J_{C,P}$ = 8.8 Hz), 151.3(t, $^2J_{C,P}$ = 6.7 Hz), 140.3 (t, $^2J_{C,P}$ = 4.7 Hz), 134.2, 133.9 (t, $^2J_{C,P}$ = 7.5 Hz), 133.7, 133.4, 133.1, 132.3, 131.0, 130.4, 130.3, 130.1 (d, $^2J_{C,P}$ = 10.1 Hz), 129.8, 129.4, 129.0, 125.1 (d, $^2J_{C,P}$ = 6.1 Hz), 118.0, 117.7, 34.8, 33.4 ppm. Elem. anal. (%) found C, 57.01; H, 4.16; N, 2.09; $C_{74}H_{60}N_2P_6Cu_2F_{12}O$ required C, 57.93; H, 3.94; N, 1.83.

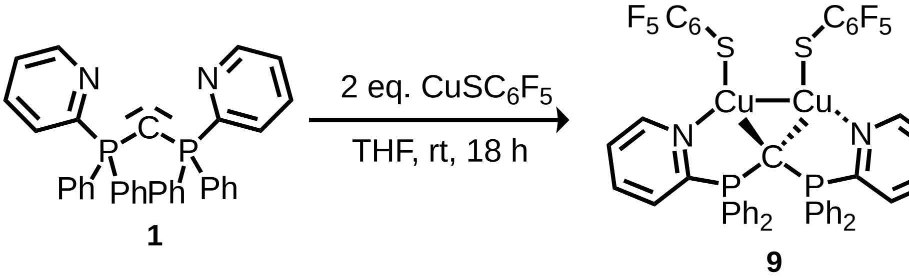
$[Cu_2(dppf)(CDP(Py)_2)](PF_6)_2$ (8)

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 $2 \cdot 5$ ml of diethyl ether and $2 \cdot 5$ ml of pentane. The light yellow residue was dried in vacuo and collected in a 90% yield (102.0 mg, 0.08 mmol). $^{31}P\{H\}$ NMR (CCl_2D_2, 101 MHz): δ 36.5 (s), –3.1 (s), 143.9 (sep.) ppm. ^{1}H NMR (CCl_2D_2, 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}), 7.53-717 (m, 30H, CH_{arom}), 7.00 (br.s, 8H, CH_{arom}), 4.45-4.21 (m, 10H, CpH) ppm. ^{13}C NMR (CCl_2D, 75 MHz): δ 155.9, 151.9, 140.9, 134.2, 133.1, 131.7, 130.3 (t, $^2J_{C,P}$ = 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; $C_{69}H_{56}N_2P_6Cu_2F_{12}Fe$ required C, 53.78; H, 3.76; N, 1.98.



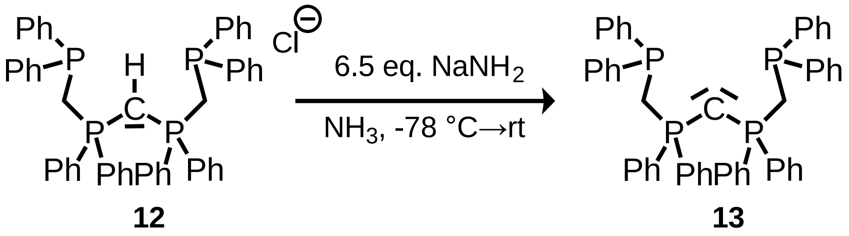
[(CuCarb)$_2$(CDP(Py)$_2$)] (11)

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): δ 22.8 ppm. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz): δ 8.50 (d, $J_{H,H}$ = 4.7 Hz, 2H, *H*6), 7.97 (dd, $J_{H,H}$ = 0.4, 7.5 Hz, 4H, *H*11), 7.94 (ddd, $J_{H,H}$ = 1.1, 8.3, 12.3 Hz, 8H, *H*8), 7.60 (ddt, $J_{H,H}$ = 1.8, 4.9, 7.7 Hz, 2H, *H*4), 7.42 (t, $J_{H,H}$ = 7.4 Hz, 4H, *H*10), 7.34-7.30 (m, 4H, *H*5,*H*3), 7.22-7.18 (m, 12H, *H*9,*H*12), 6.95 (dt, $J_{H,H}$ = 1.3, 7.0 Hz, 4H, *H*13), 6.95 (dt, $J_{H,H}$ = 0.9, 7.3 Hz, 4H, *H*14) ppm. ^{13}C NMR (CCl$_2$D, 75 MHz): δ 155.4-154.2(m, *C*2), 151.2 (s, *C*16), 150.6 (t, $^2J_{C,P}$ = 8.3 Hz, *C*6), 137.9 (t, $^2J_{C,P}$ = 5.1 Hz, *C*4), 133.8 (t, $^2J_{C,P}$ = 4.8 Hz, *C*8), 132.8 (s, *C*10), 129.3 (t, $^2J_{C,P}$ = 5.9 Hz, *C*9), 128.6-127.7 (m, *C*3,*C*7), 126.7 (s, *C*5), 124.5 (s, *C*15), 123.5 (s, *C*13), 119.6 (s, *C*11), 115.3 (s, *C*12), 114.9 (s, *C*13), –0.9 (t, $^2J_{C,P}$ = 54.0 Hz, *C*1) ppm. LIFDI-HRMS: *m/z* 539.18016. [M-H]$^+$. Elem. anal. (%) found C, 70.68; H, 4.44; N, 5.61; $C_{59}H_{44}N_4P_2Cu_2$ required C, 71.00; H, 4.66; N, 5.01.



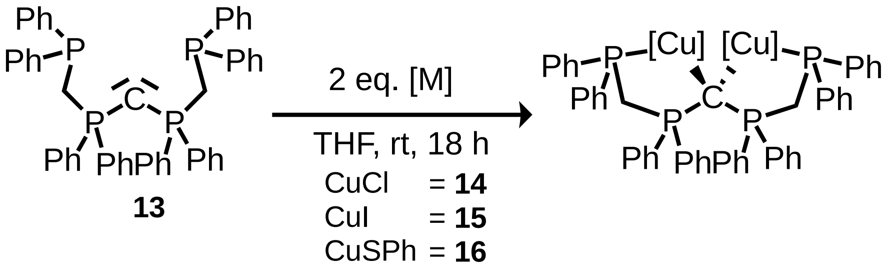
[(CuS(C$_6$F$_5$))$_2$(CDP(Py)$_2$)] (9)

A 76.0 mg portion (0.14 mmol, 1 eq.) of **1** and 74.0 mg (0.28 mmol, 2 eq.) of cupper(I) pentafluorothiophenolate 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): δ 23.1 ppm. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz): δ 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, C*H*$_{arom}$), 7.27-7.12 (m, 5H, C*H*$_{arom}$) ppm. Elem. anal. (%) found C, 42.47; H, 2.24; N, 2.28; $C_{47}H_{28}P_4F_{22}N_2S_2$ required C, 41.70; H, 2.08; N, 2.07.



(CDP(CH_2PPh_2)$_2$ (13)

A 250.0 mg portion (0.30 mmol, 1.0 eq.) of [CH(dppm)$_2$]Cl[3,7] (**12**) and 80.4 mg $NaNH_2$ (2.1 mmol, 6.5 eq.) were suspended in NH_3 (l.) at −78 °C and stirred till the temperature reached room temperature, causing the NH_3 to vaporize. The light yellow residue was disolved in toluene and the feed was removed via filtration. The solvent was then evaporated and the precipitate was washed with 2 · 15 ml of pentane. The yellow residue was dried in vacuo and collected in a 98% yield (233.1 mg, 0.30 mmol). $^{31}P\{H\}$ NMR (C_6D_6, 101 MHz): δ 23.2 (dt, J = 8.0, 14.7 Hz), −15.8 (d, J = 118.5 Hz) ppm. ^1H NMR (CCl_2D_2, 300 MHz): δ 7.09-7.71 (m, 8H, C*H*$_{arom}$), 7.51-7.31 (m, 8H, C*H*$_{arom}$), 7.08-6.88 (m, 24H, C*H*$_{arom}$), 3.44 (br.s, 3H, C*H*/C*H*$_2$), 1.44 (s, 1H, C*H*) ppm. APCI-HRMS: *m/z* 781.24799 [M+H]$^+$. Elem. anal. (%) found C, 77.99; H, 5.74; $C_{51}H_{44}P_4$ required C, 78.45; H, 5.68.



[(CuCl)$_2$(CDP(CH_2PPh_2)$_2$] (14)

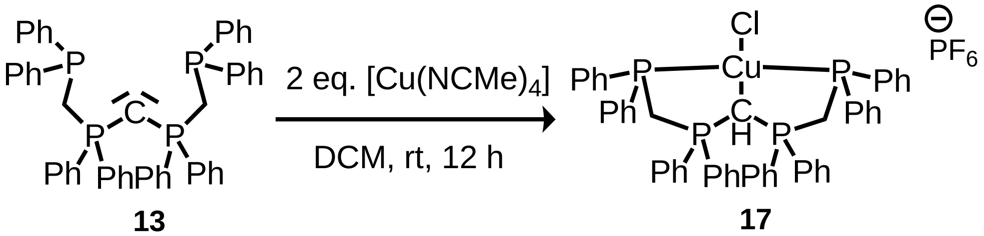
A 50.0 mg portion (0.06 mmol, 1 eq.) of **13** and 12.9 mg (0.12 mmol, 2 eq.) of cupper(I) chloride were suspended in 5.0 ml THF at room temperature and stirred for 1 h. The solvent was then evaporated and the precipitate was washed with 3 · 15 ml of diethyl ether and 2 · 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 77% yield (48.1 mg, 0.05 mmol). $^{31}P\{H\}$ NMR (CCl_2D_2, 101 MHz): δ 20.4 (dd, J = 34.6, 49.9 Hz), −32.2-−32.9 (m) ppm. ^{31}P-^1H NMR (CCl_2D_2, 101 MHz): δ 20.1 (m), −32.5 (m) ppm. ^1H NMR (CCl_2D_2, 300 MHz): δ 7.45 (m, 18H, C*H*$_{arom}$), 7.18 (m, 16H, C*H*$_{arom}$), 6.95 (m, 6H, C*H*$_{arom}$), 6.79 (br.s, 6H, C*H*$_{arom}$), 4.06 (br.s, 4H, 2 · C*H*$_2$) ppm. APCI-HRMS: *m/z* 941.07087 [M-Cl]$^+$.

[(CuI)$_2$(CDP(CH_2PPh_2)$_2$] (15)

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 · 15 ml of diethyl ether and 2 · 15 ml of pentane. The light orange residue was dried in vacuo and collected in a 83% yield (62.0 mg, 0.05 mmol). ^{31}P{H} NMR (CCl$_2$D$_2$, 101 MHz): δ 22.2 (dd, J = 36.9, 55.4 Hz), –37.6-–38.2 (m) ppm. ^{31}P-^{1}H NMR (CCl$_2$D$_2$, 101 MHz): δ 22.5 (m), –38.0 (m) ppm. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz): δ 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-CuI+H]$^+$, 781.2461 [M-(CuI)$_2$+H]$^+$.

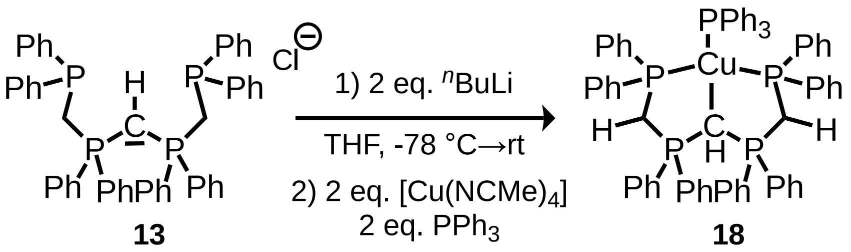
[(CuSPh)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (16)

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 · 15 ml of diethyl ether and 2 · 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{H} NMR (CCl$_2$D$_2$, 101 MHz): δ 19.8-19.0 (m), –33.1-–33.9 ppm. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz): δ 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 · 15 ml of diethyl ether and 2 · 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{H} NMR (CCl$_2$D$_2$, 101 MHz): δ 20.8-19.2 (m), –29.6-–30.4 (m), –32.0-–33.0 (m) ppm. ^{19}F{H} NMR (CCl$_2$D$_2$, 282 MHz): δ 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 ^{n}BuLi in hexane (2.5 M, 0.24 mmol, 2.0 eq.) at –78 °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 · 5 ml of diethyl ether and 2 · 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_2D_2, 101 MHz): δ 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. ^1H NMR (CCl_2D_2, 300 MHz): δ 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 · CH) ppm. Elem. anal. (%) found C, 74.67; H, 5.19; $C_{69}H_{59}P_5Cu$ required C, 74.89; H, 5.37.

NMR spectroscopy

[(CuCl)$_2$(CDP(Py)$_2$)] (2)

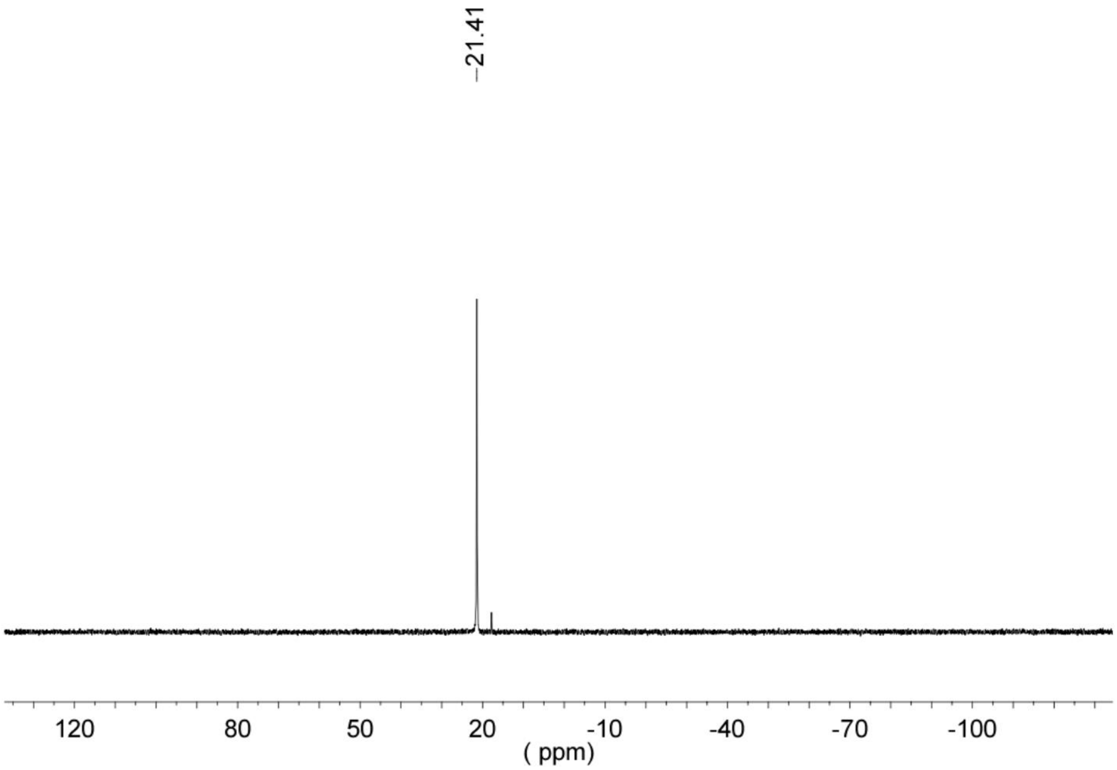


Figure S-1. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [(CuCl)$_2$(CDP(Py)$_2$)] (**2**).

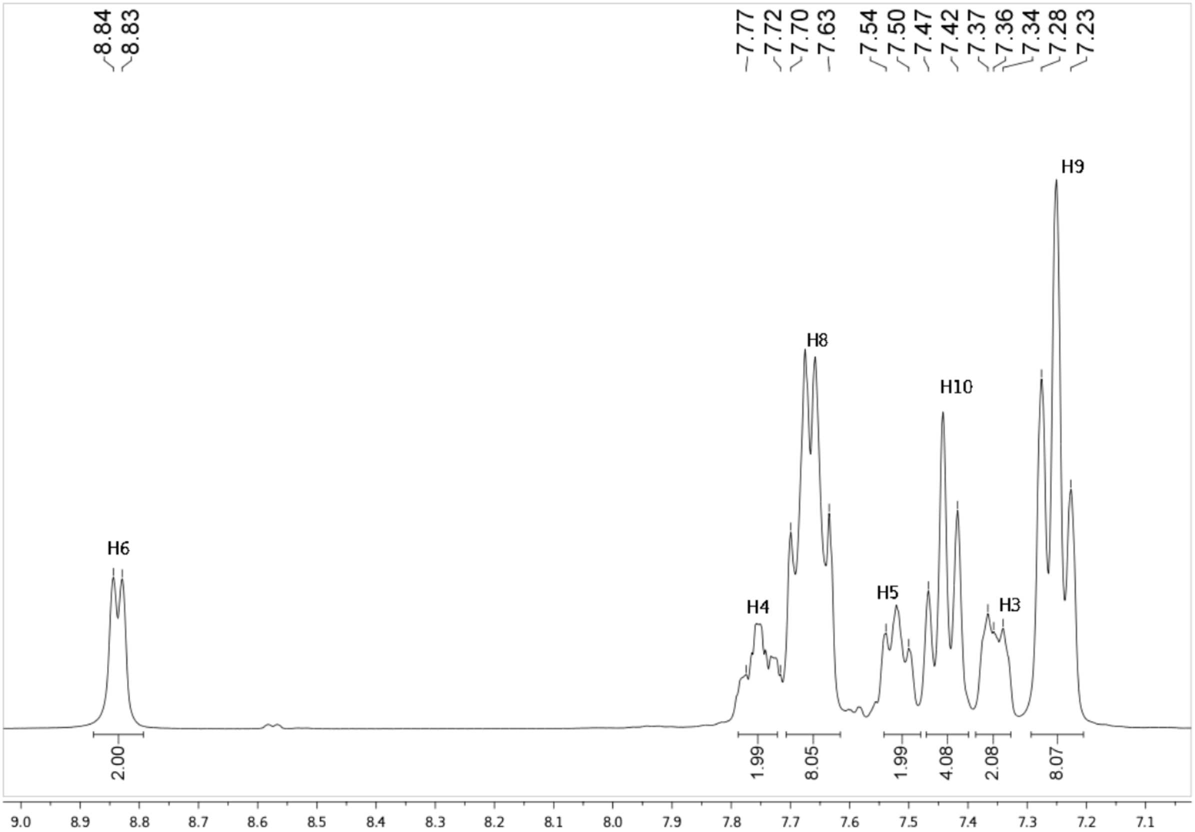


Figure S-2. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [$(CuCl)_2(CDP(Py)_2)$] (**2**).

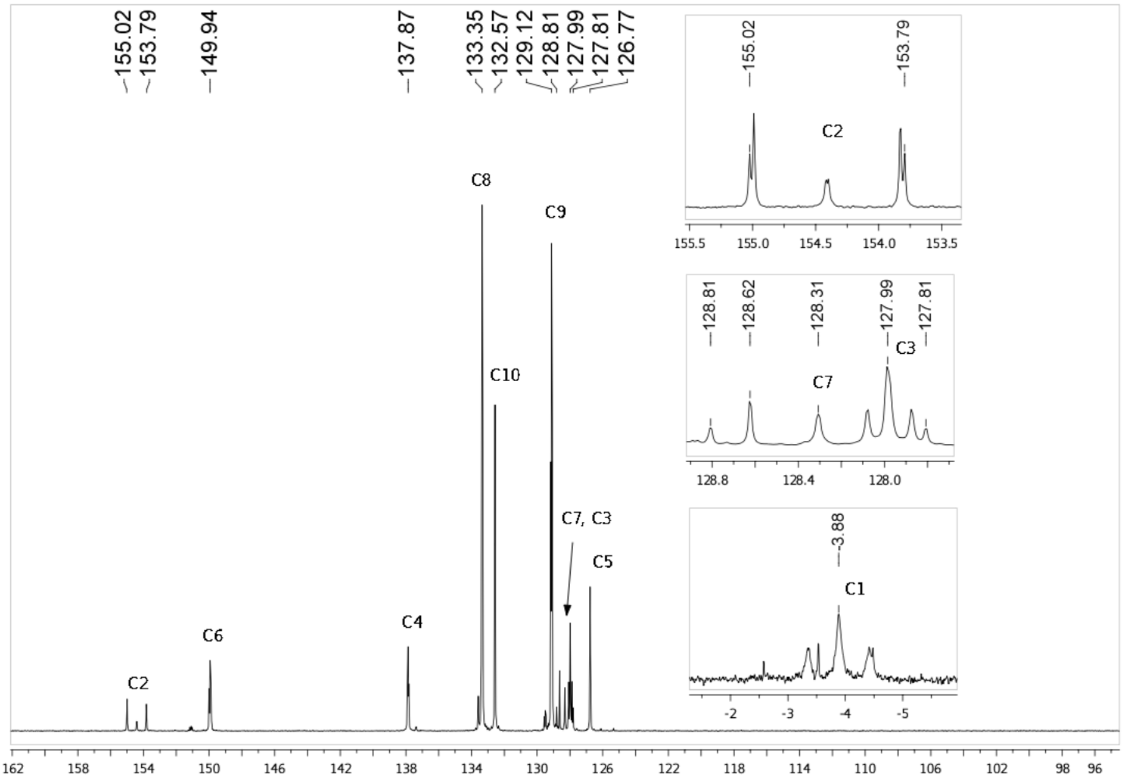


Figure S-3. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of [$(CuCl)_2(CDP(Py)_2)$] (**2**).

[(CuI)$_2$(CDP(Py)$_2$)] (3)

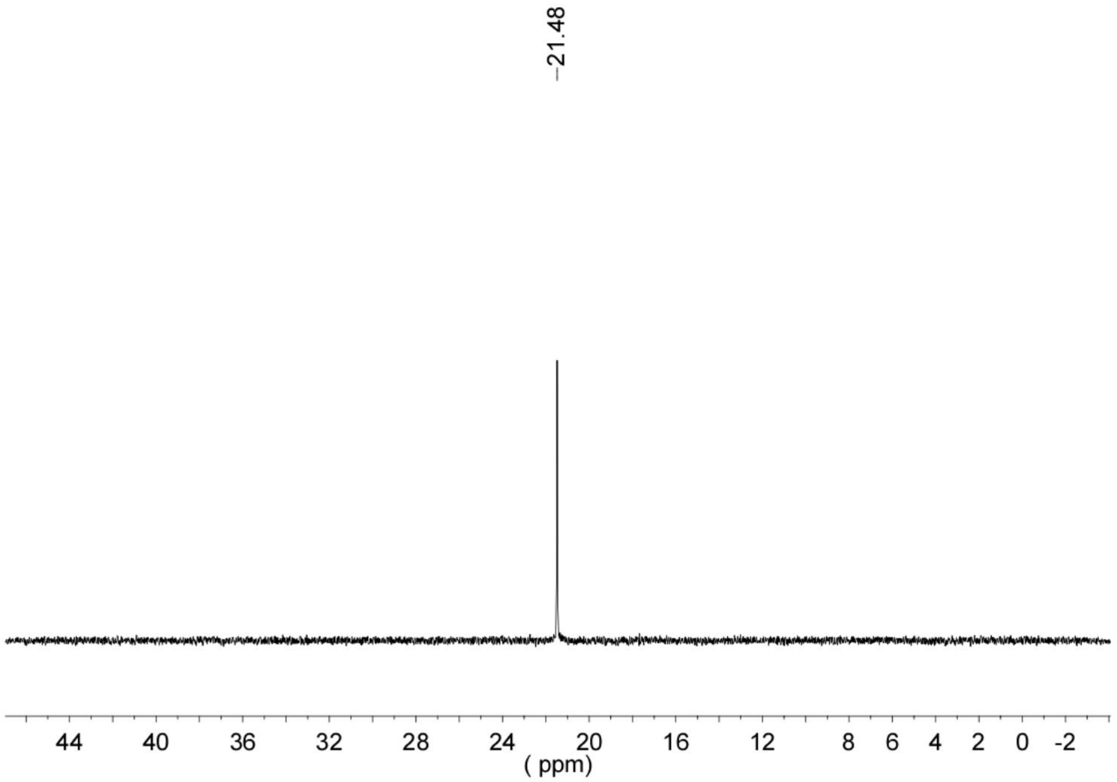


Figure S-4. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuI)$_2$(CDP(Py)$_2$)] (**3**).

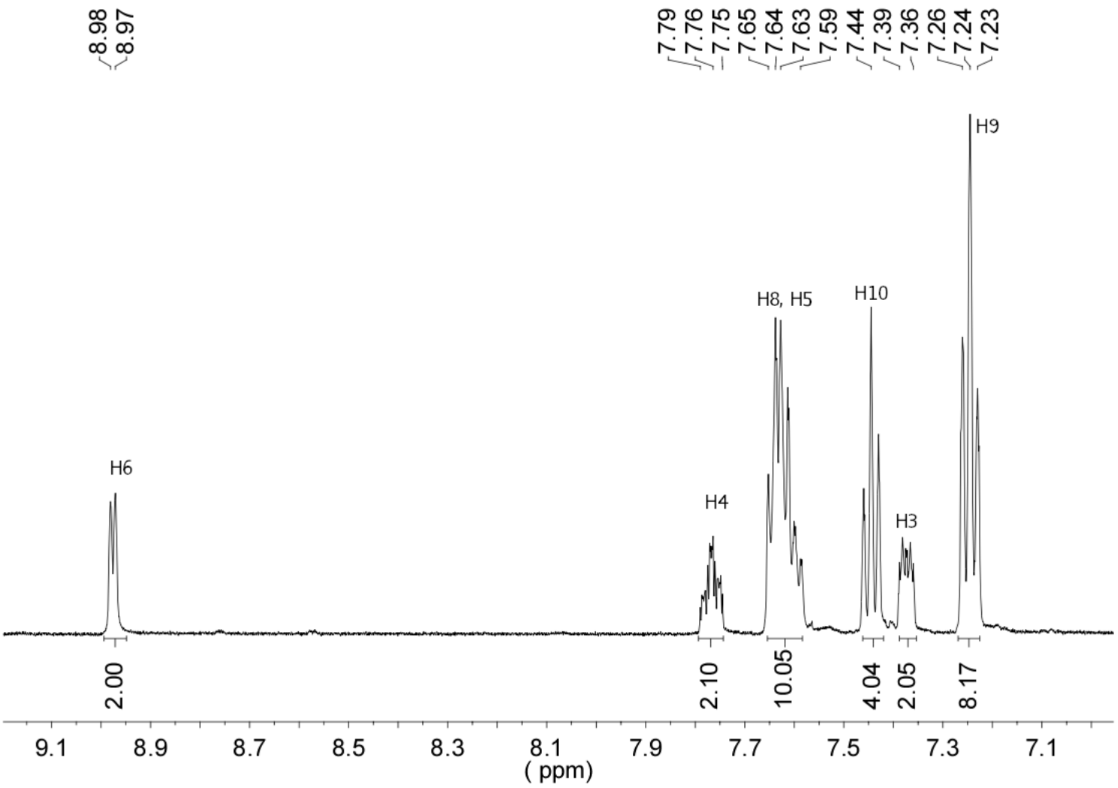


Figure S-5. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [$(CuI)_2(CDP(Py)_2)$] (**3**).

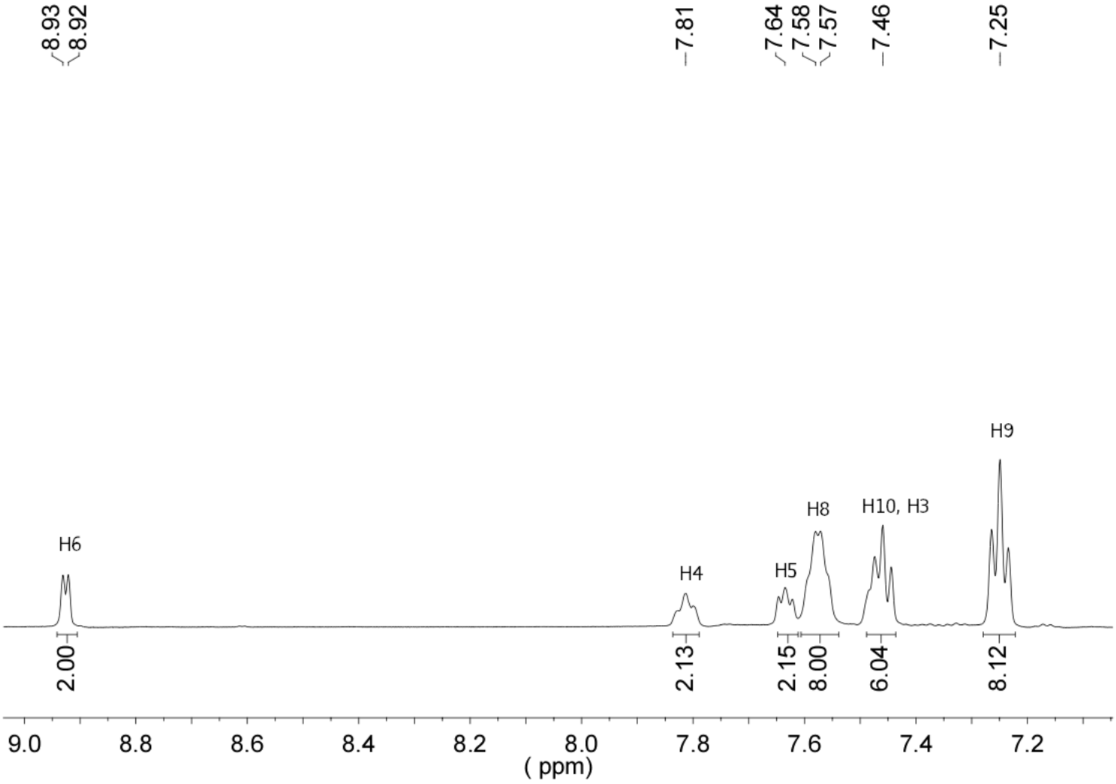


Figure S-6. ^{1}H NMR (CCl_2D_2, 200 K, 300 MHz, [ppm]) of [$(CuI)_2(CDP(Py)_2)$] (**3**).

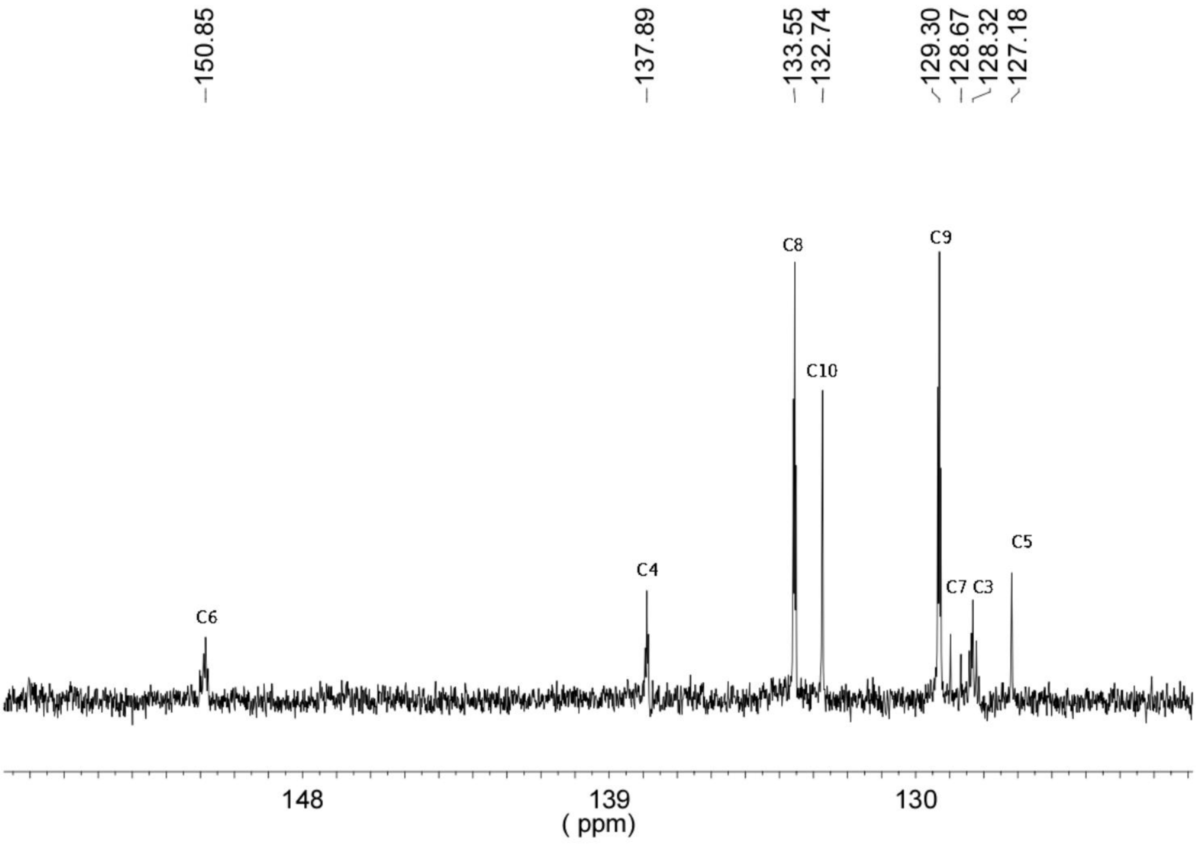


Figure S-7. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of [$(CuI)_2(CDP(Py)_2)$] (**3**).

[(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (4)

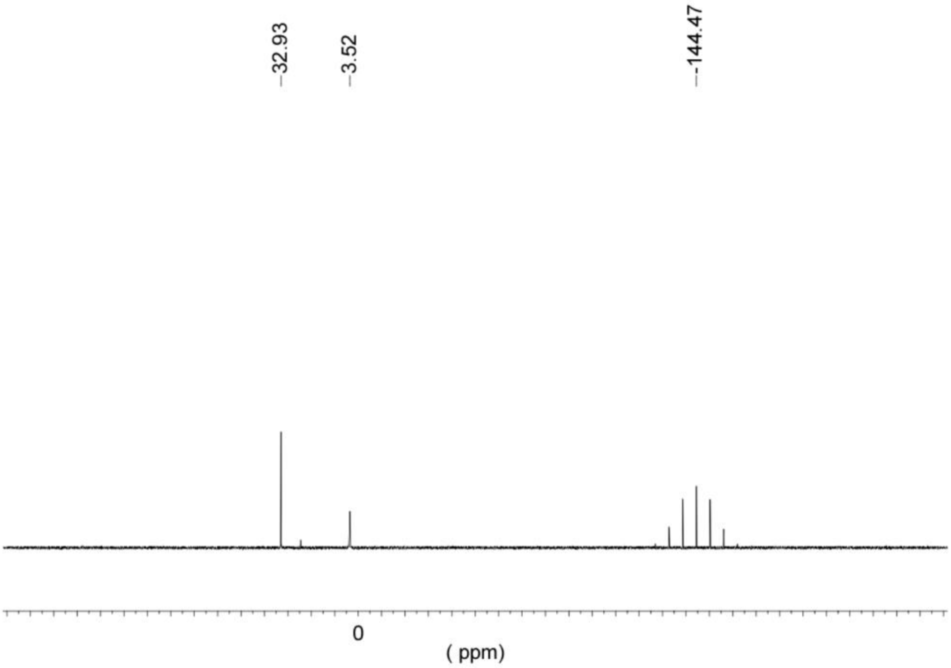


Figure S-8. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (**4**).

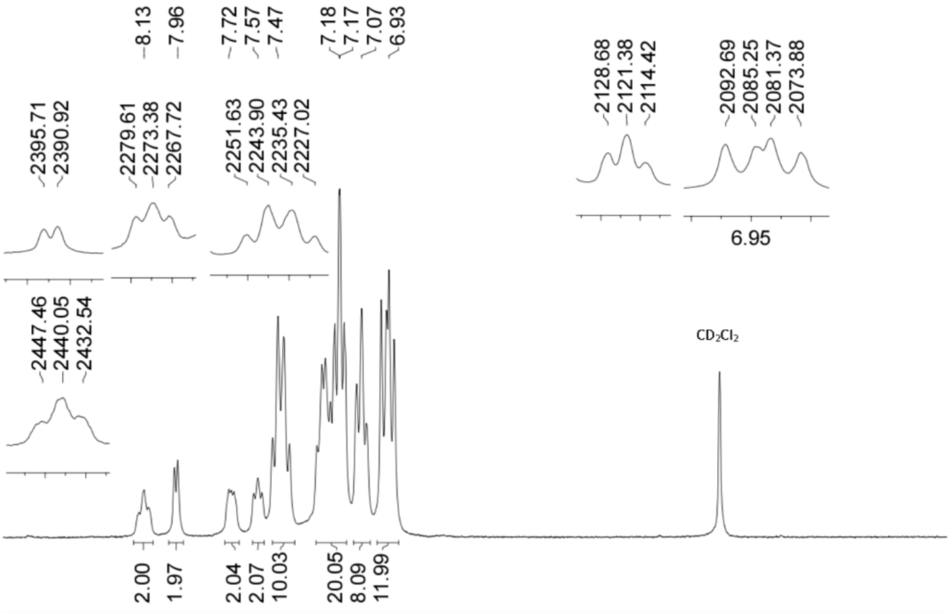


Figure S-9. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuPPh$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (**4**).

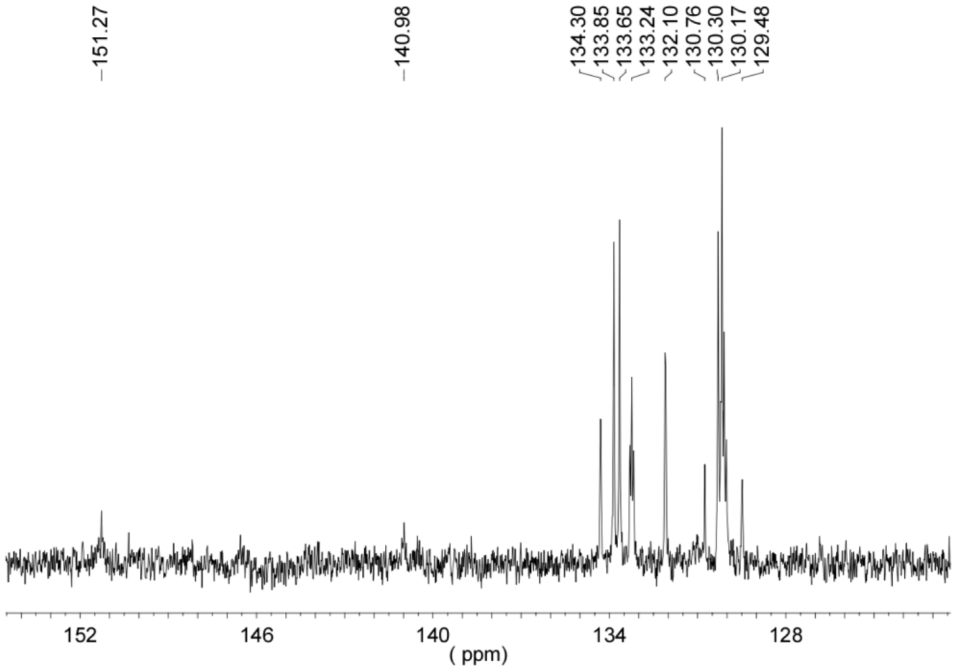


Figure S-10. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of $[(CuPPh_3)_2(CDP(Py)_2)](PF_6)_2$ (**4**).

$[(Cu(PPhOMe)_3)_2(CDP(Py)_2)](PF_6)_2$ (5)

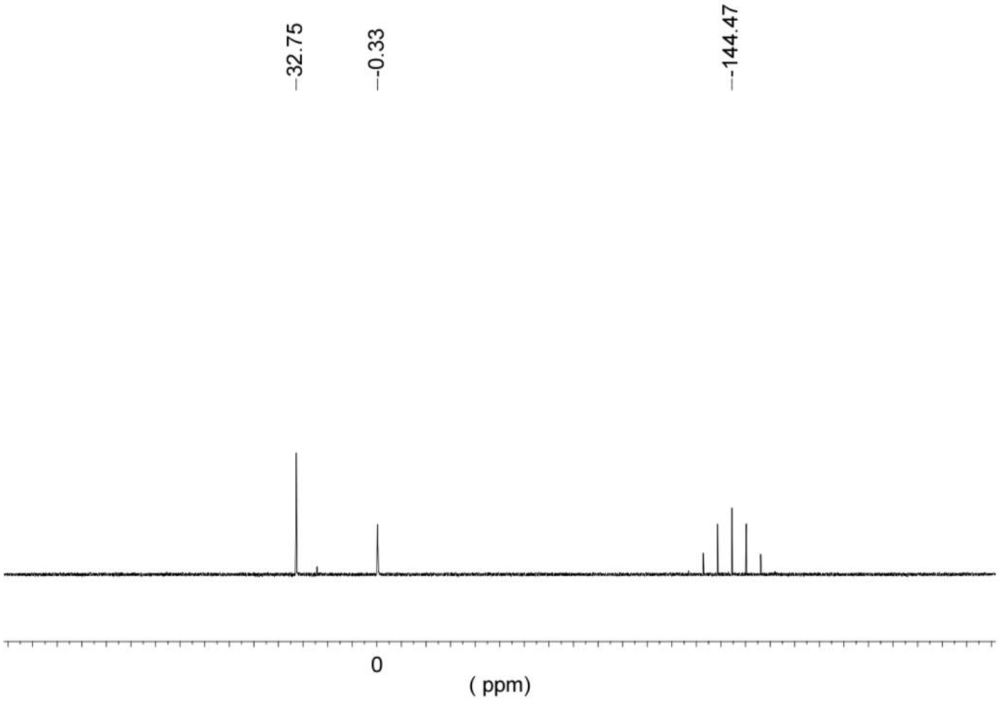


Figure S-11. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of $[(Cu(PPhOMe)_3)_2(CDP(Py)_2)](PF_6)_2$ (**5**).

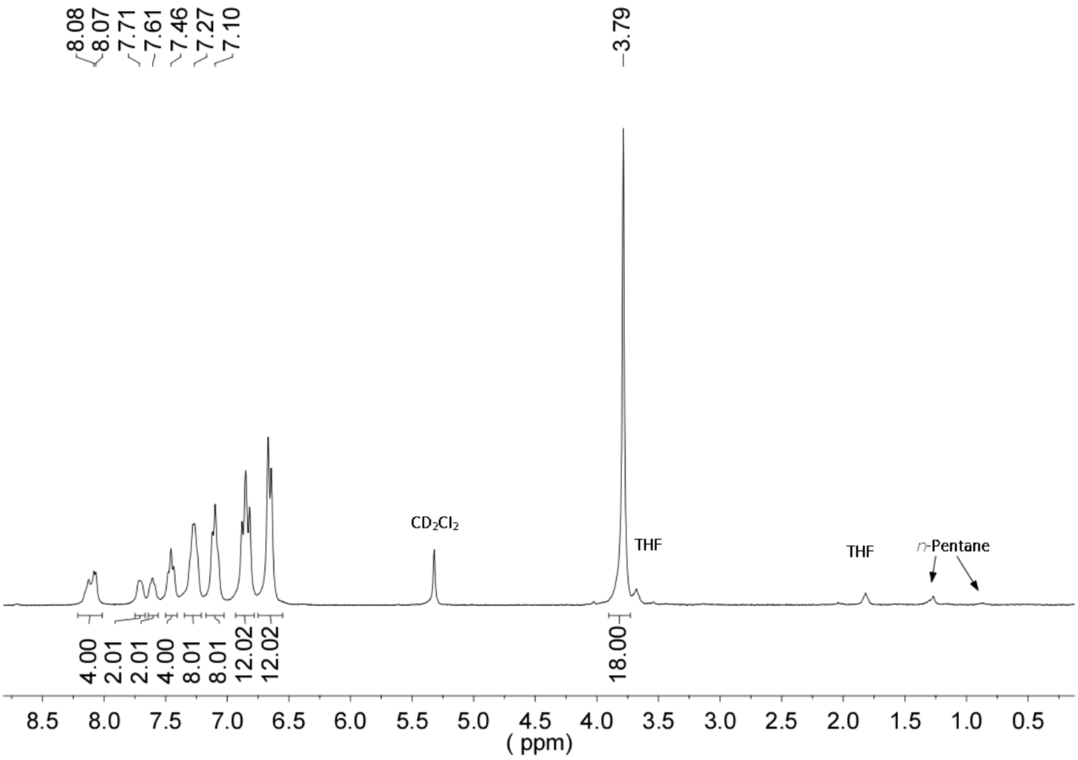


Figure S-12. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [(Cu(PPhOMe)$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (**5**).

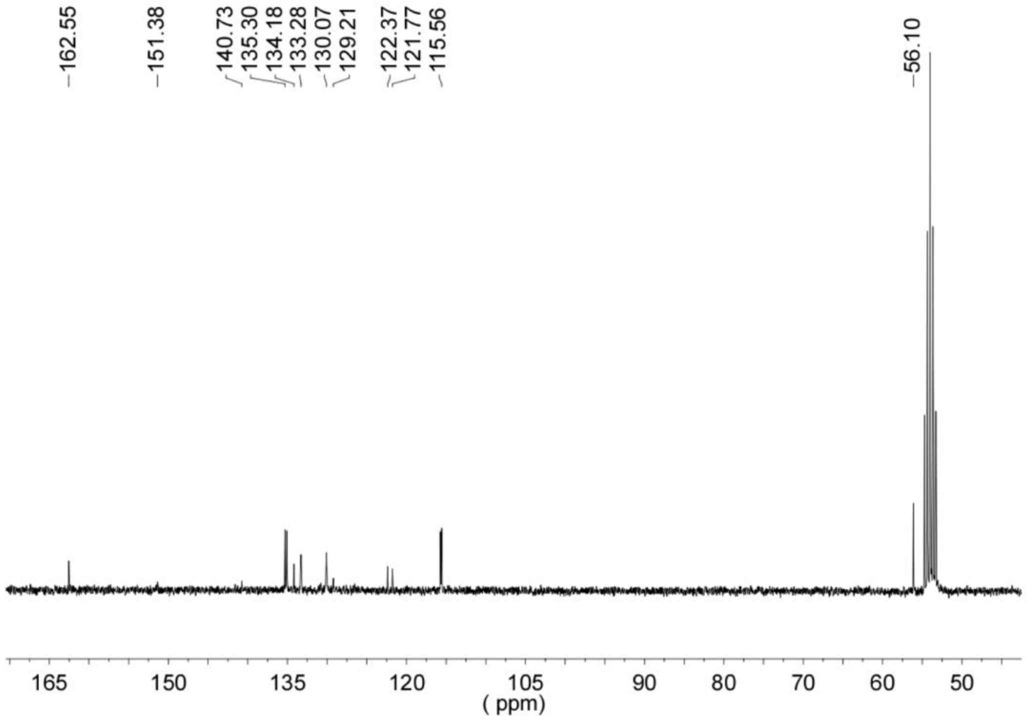


Figure S-13. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of [(Cu(PPhOMe)$_3$)$_2$(CDP(Py)$_2$)](PF$_6$)$_2$ (**5**).

[Cu2(DPEPhos)(CDP(Py)2)](PF6)2 (6)

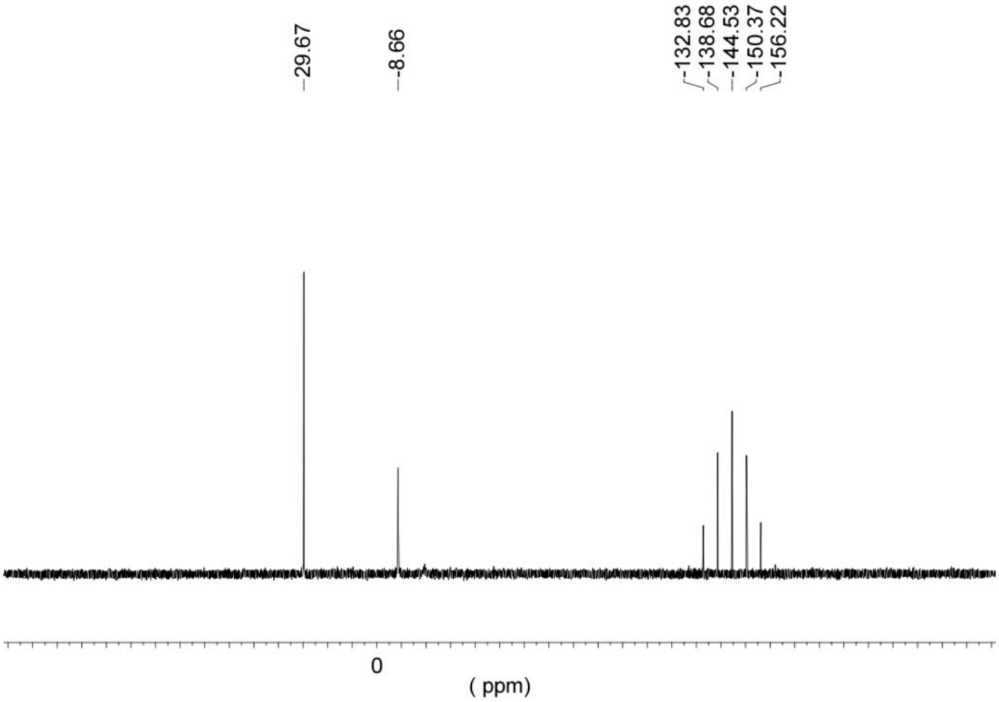


Figure S-14. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [Cu_2(DPEPhos)(CDP($Py)_2$)]($PF_6)_2$ (**6**).

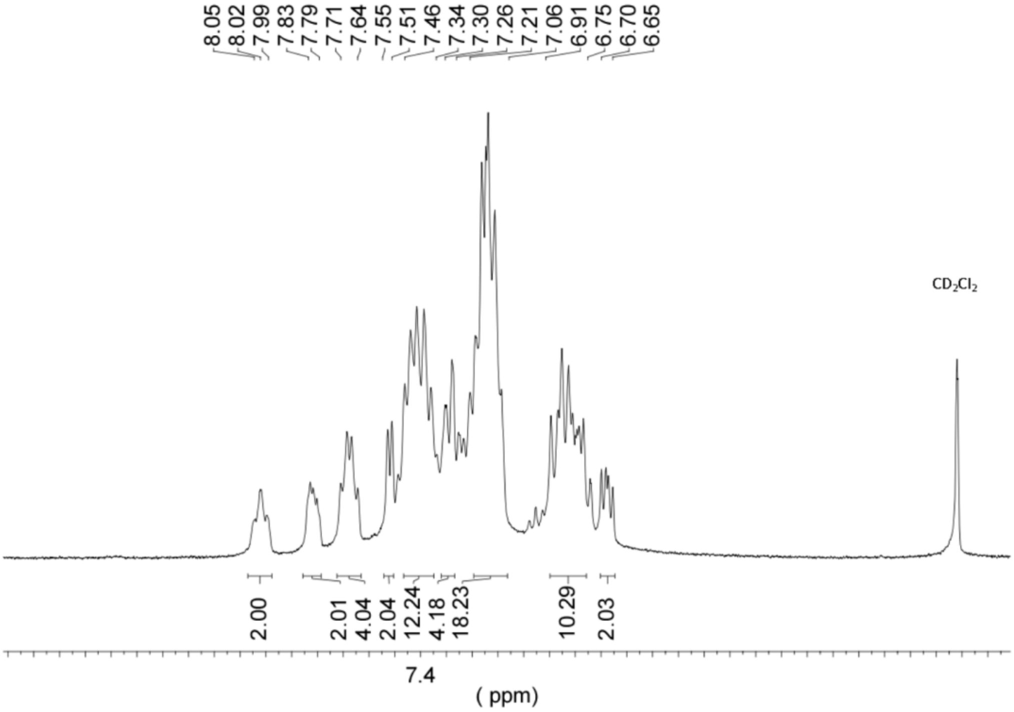


Figure S-15. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [Cu_2(DPEPhos)(CDP($Py)_2$)]($PF_6)_2$ (**6**).

$[Cu_2(XantPhos)(CDP(Py)_2)](PF_6)_2$ (7)

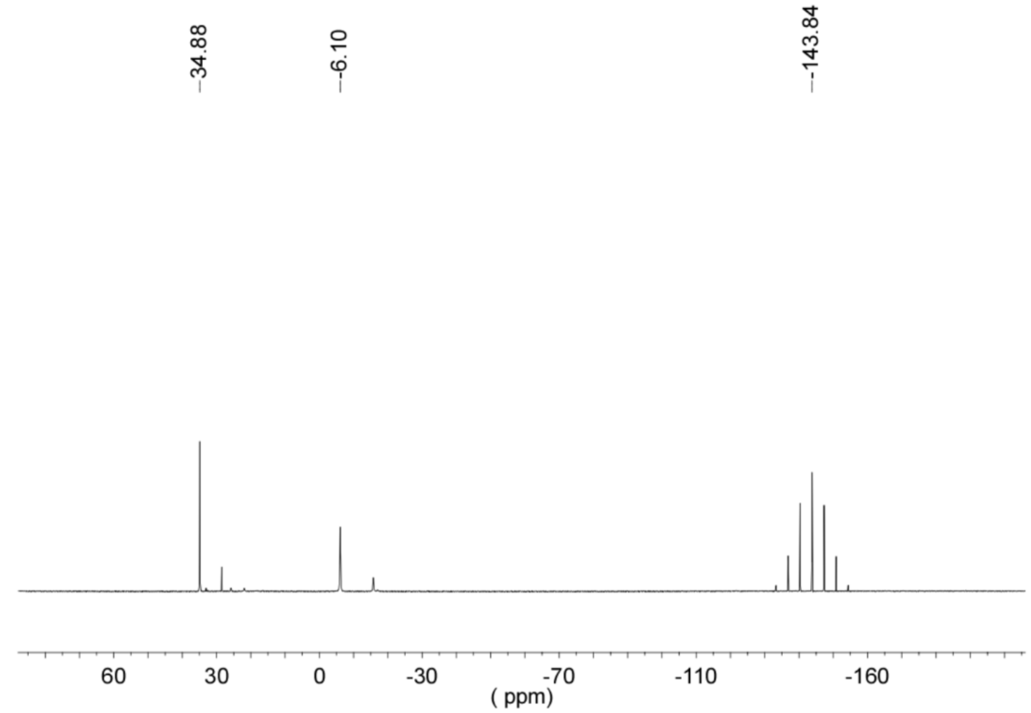


Figure S-16. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of $[Cu_2(XantPhos)(CDP(Py)_2)](PF_6)_2$ (**7**).

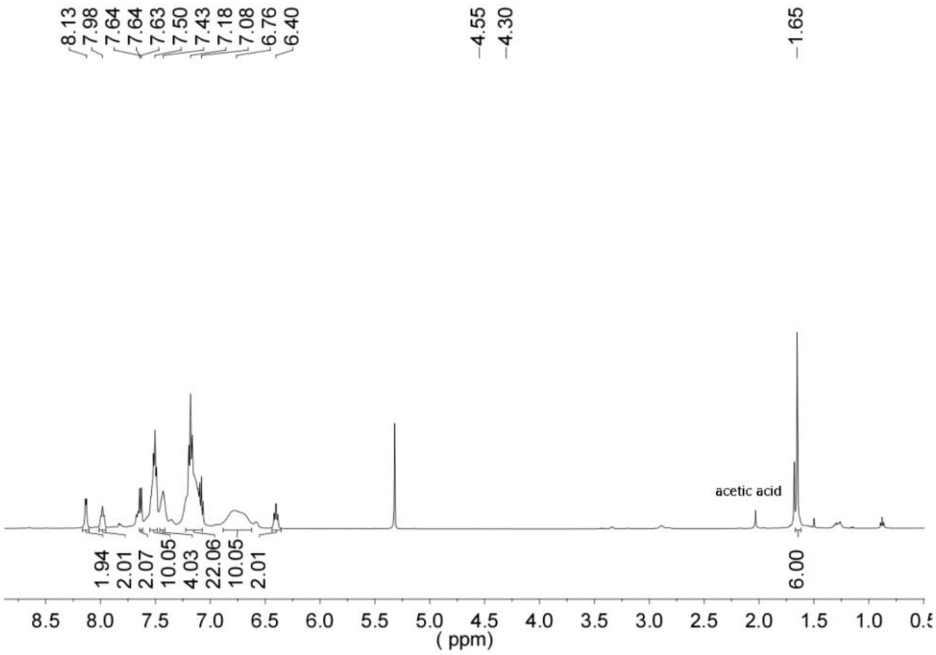


Figure S-17. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of $[Cu_2(XantPhos)(CDP(Py)_2)](PF_6)_2$ (**7**).

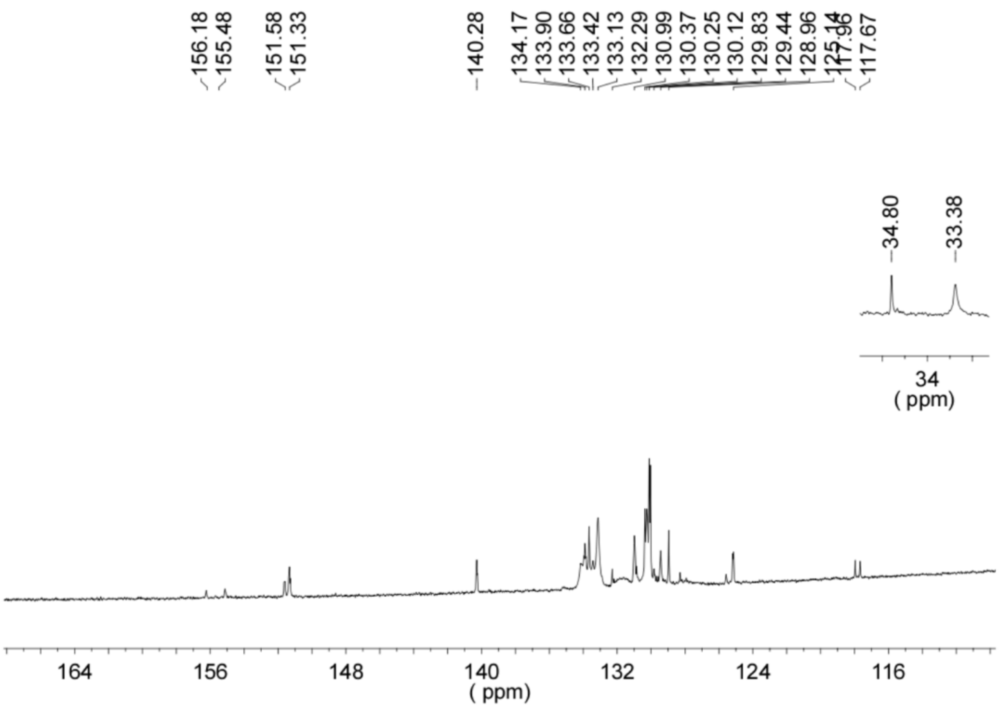


Figure S-18. ^{13}C NMR (CCl$_2$D$_2$, 75 MHz, [ppm]) of [Cu$_2$(XantPhos)(CDP(Py)$_2$)](PF$_6$)$_2$ (**7**).

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

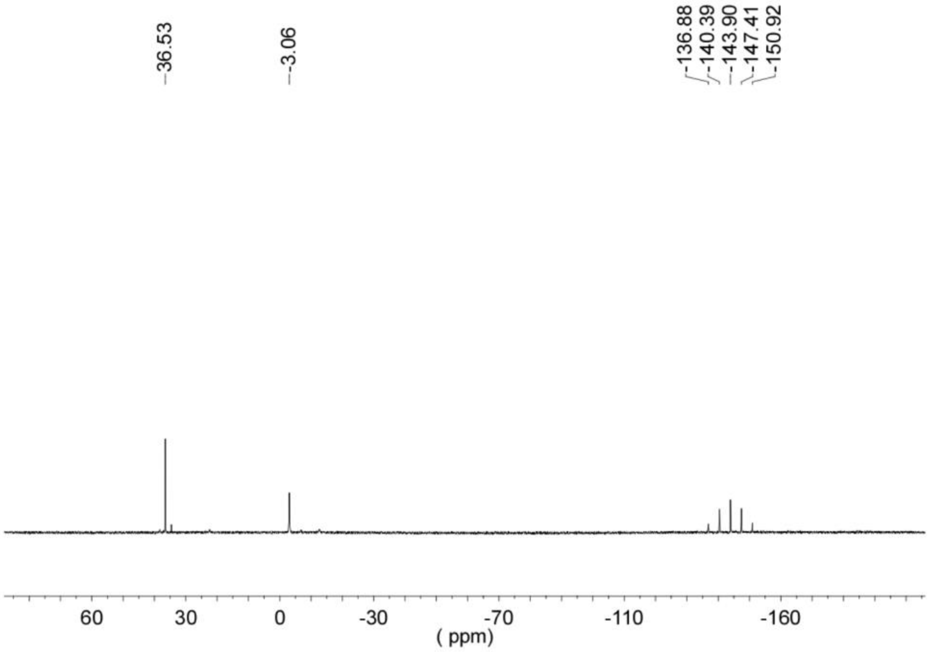


Figure S-19. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [Cu$_2$(dppf)(CDP(Py)$_2$)](PF$_6$)$_2$ (**8**).

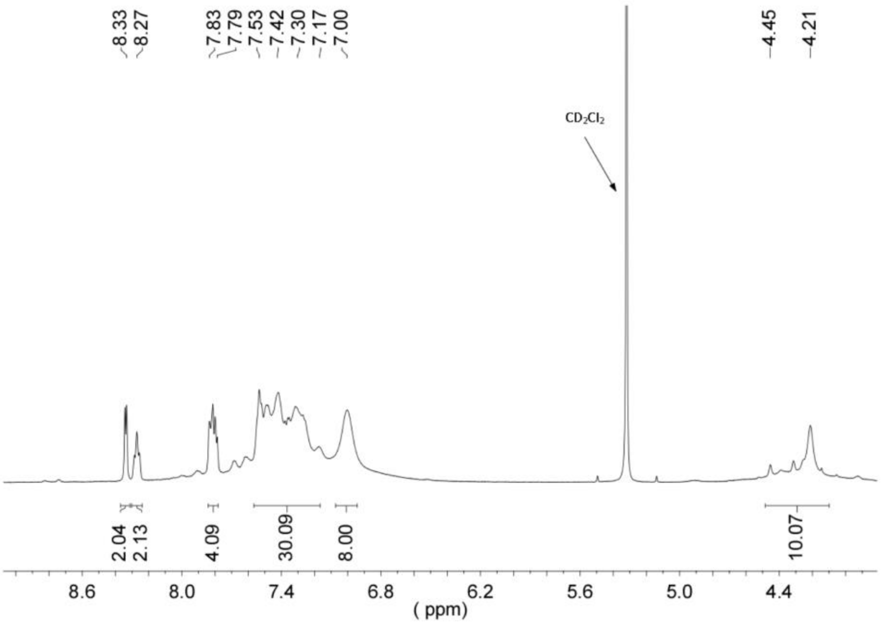


Figure S-20. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [Cu_2(dppf)(CDP(Py)$_2$)](PF_6)$_2$ (**8**).

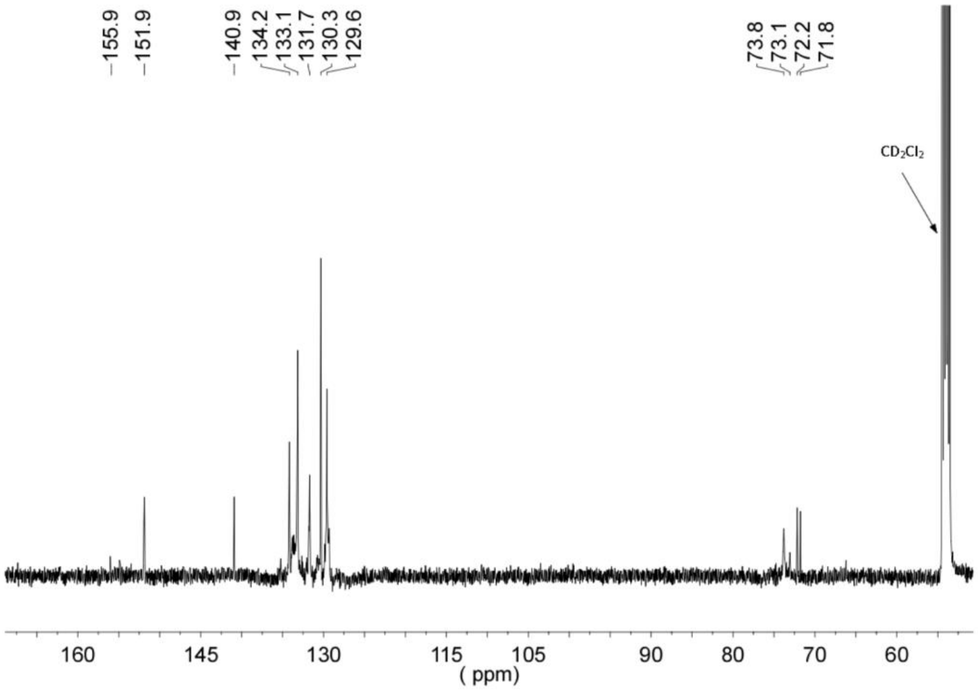


Figure S-21. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of [Cu_2(dppf)(CDP(Py)$_2$)](PF_6)$_2$ (**8**).

[(CuCarb)$_2$(CDP(Py)$_2$)] (11)

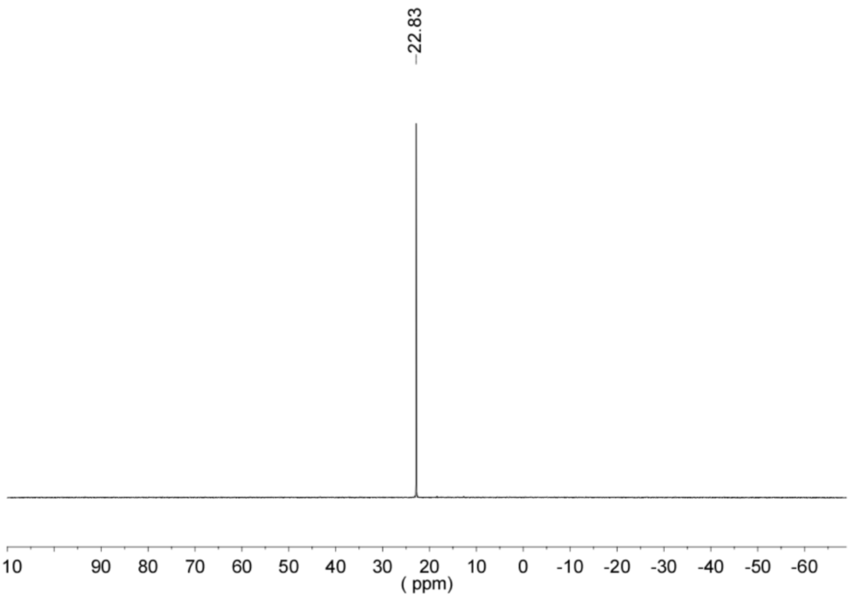


Figure S-22. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (**11**).

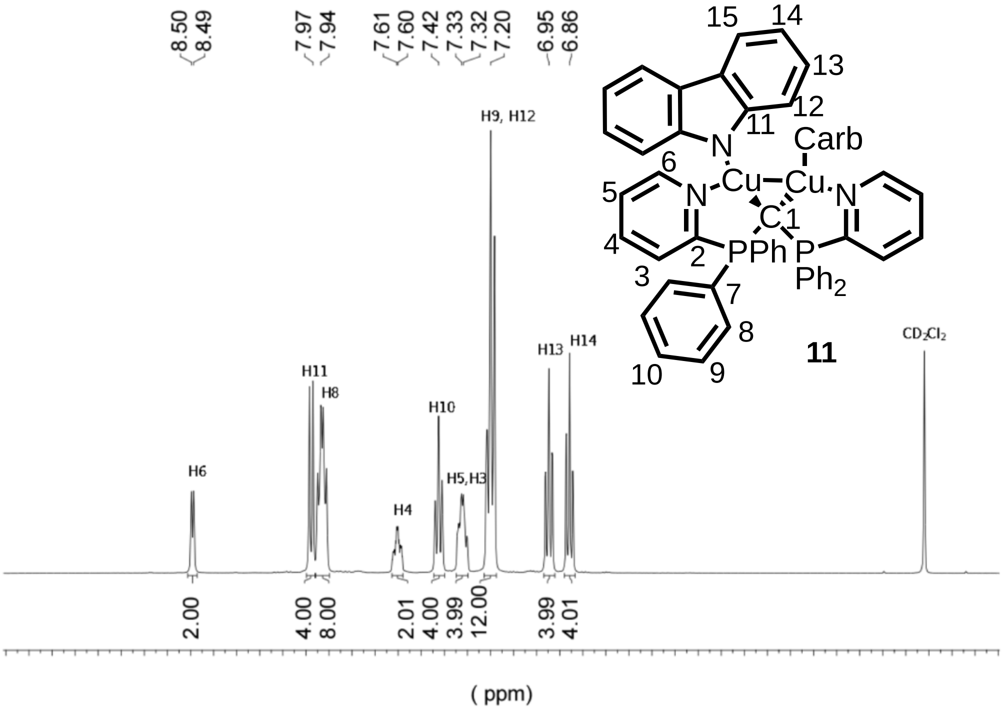


Figure S-23. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (**11**).

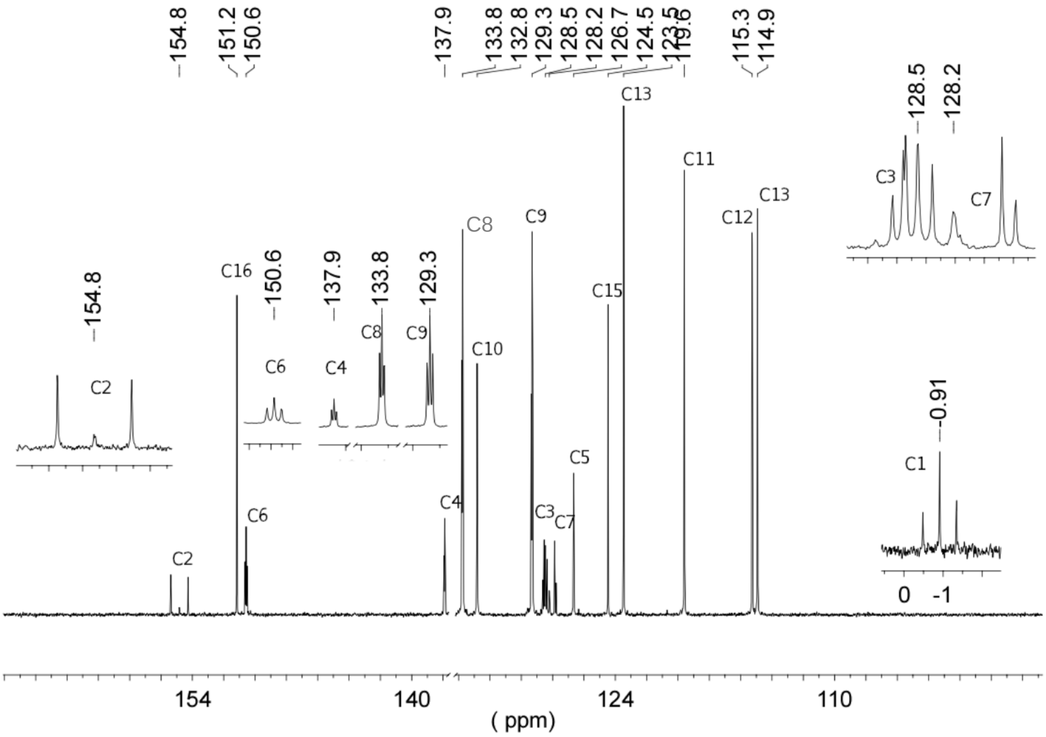


Figure S-24. ^{13}C NMR (CCl_2D_2, 75 MHz, [ppm]) of [(CuCarb)$_2$(CDP(Py)$_2$)] (**11**).

[(CuS(C$_6$F$_5$))$_2$(CDP(Py)$_2$)] (9)

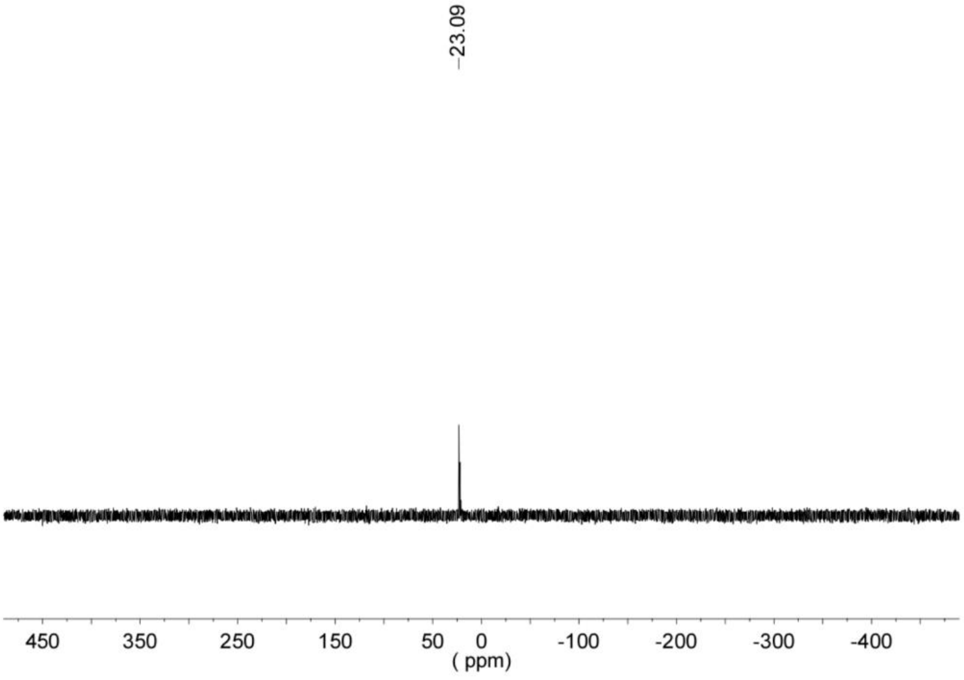


Figure S-25. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [(CuS(C$_6$F$_5$))$_2$(CDP(Py)$_2$)] (**9**).

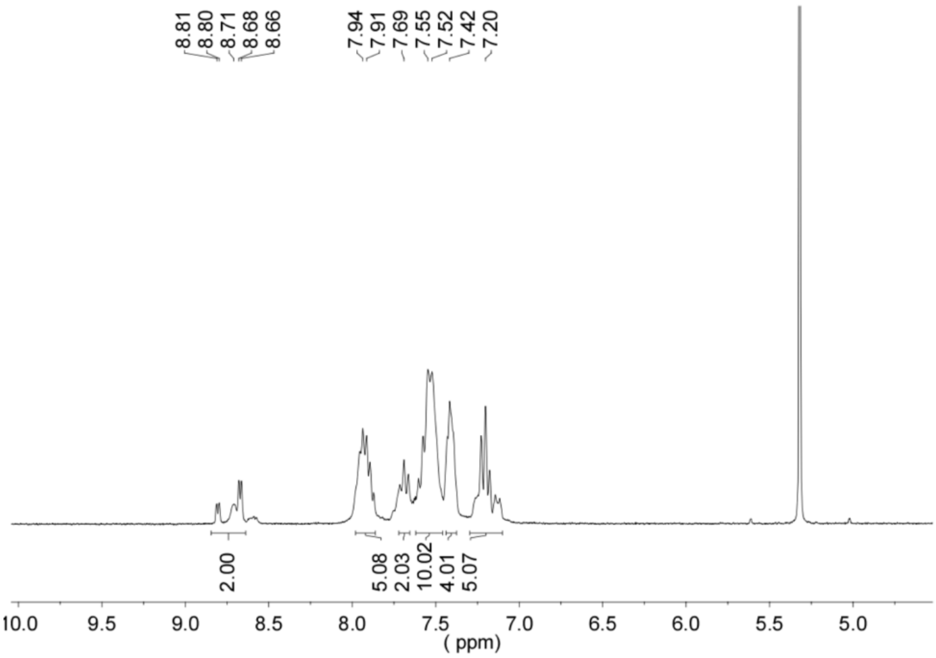


Figure S-26. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [$(CuS(C_6F_5))_2(CDP(Py)_2)$] (**9**).

($CDP(CH_2PPh_2)_2$ (13)

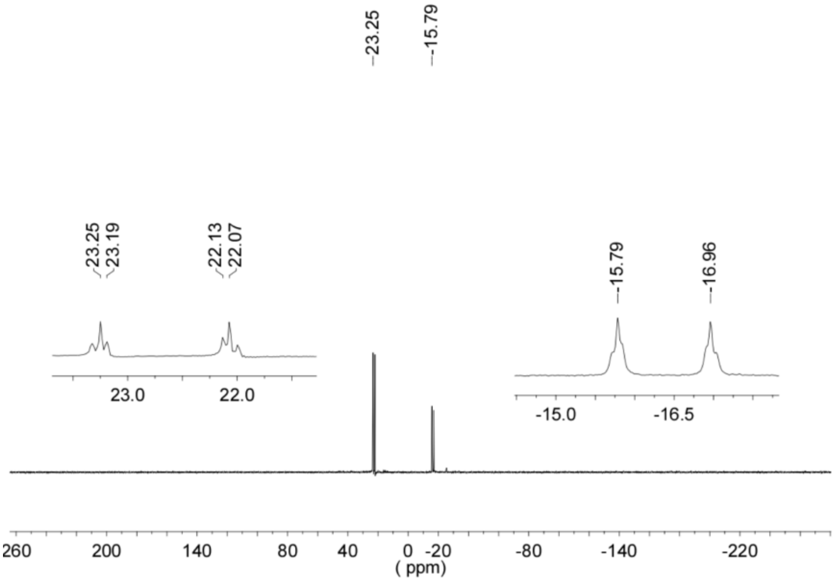


Figure S-27. ^{31}P NMR (Toluol, 101 MHz, [ppm]) of ($CDP(CH_2PPh_2)_2$ (**13**).

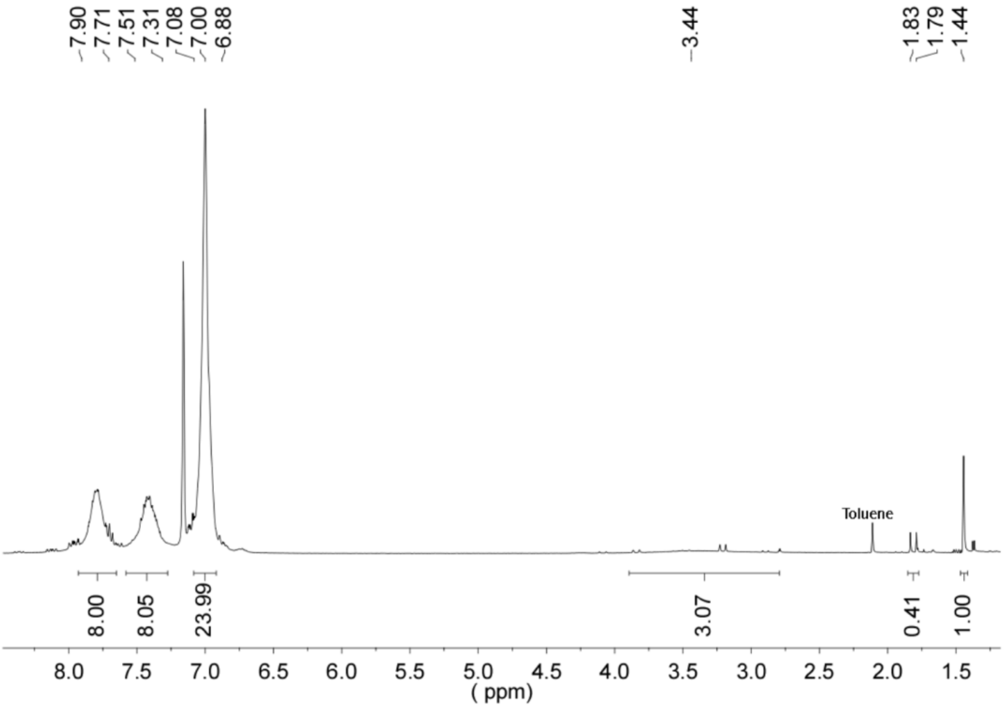


Figure S-28. ^{1}H NMR (C_6D_6, 300 MHz, [ppm]) of (CDP(CH_2PPh_2)$_2$ (**13**).

[$(CuCl)_2$(CDP(CH_2PPh_2)$_2$] (14)

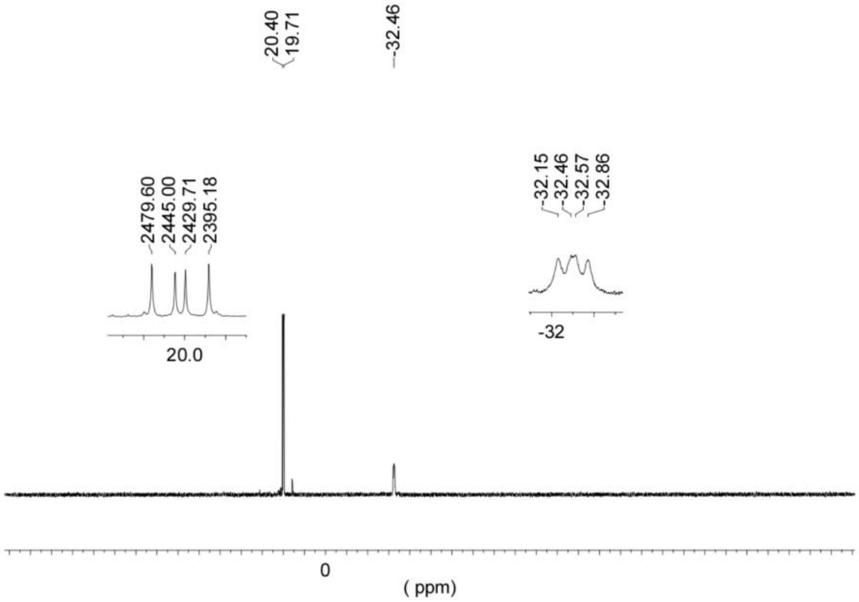


Figure S-29. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [$(CuCl)_2$(CDP(CH_2PPh_2)$_2$] (**14**).

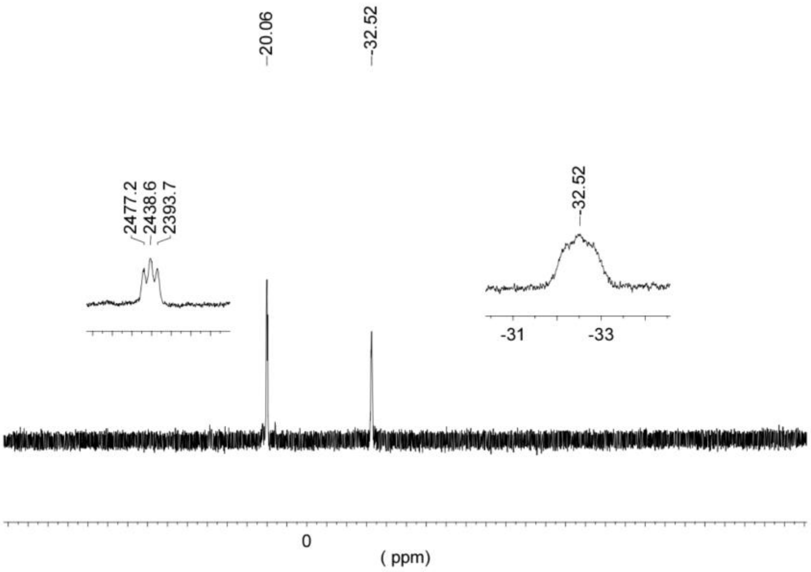


Figure S-30. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuCl)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (**14**).

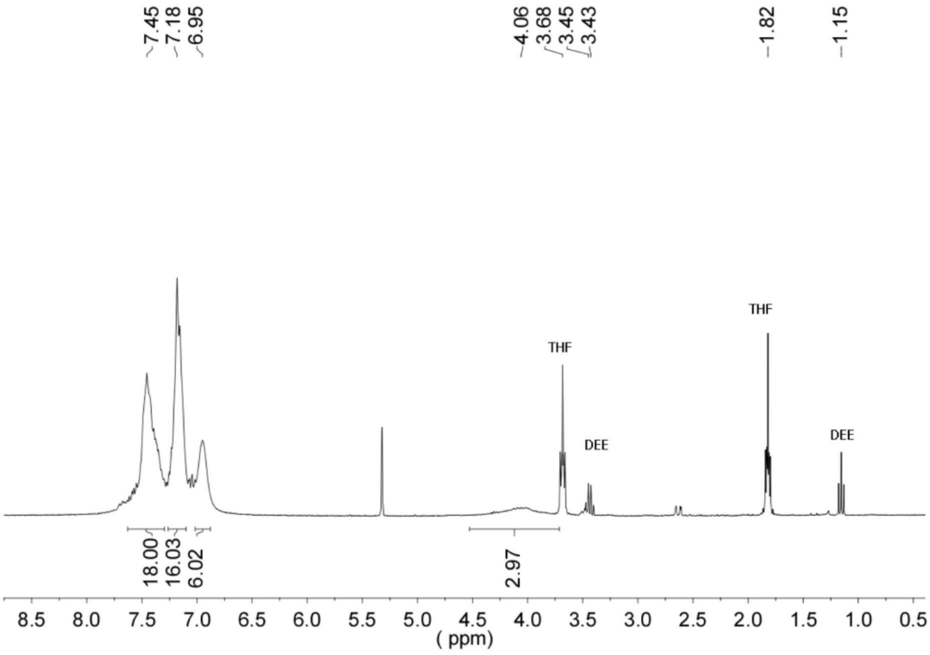


Figure S-31. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuCl)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (**14**).

[(CuI)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (15)

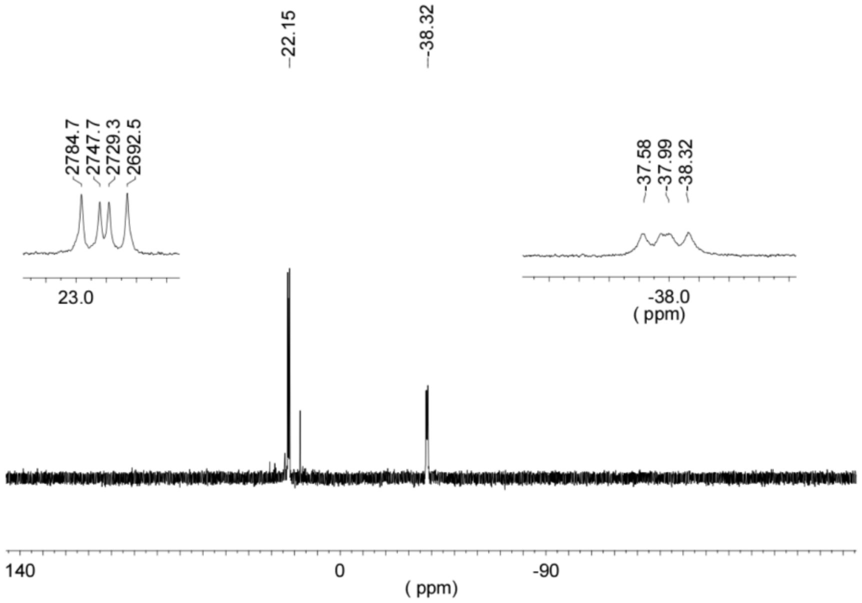


Figure S-32. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuI)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (**15**).

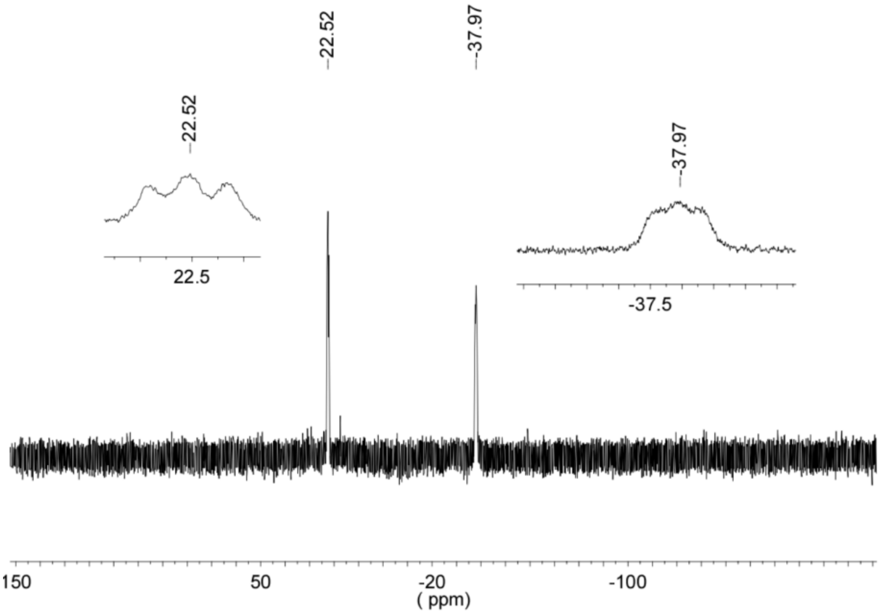


Figure S-33. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [(CuI)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (**15**).

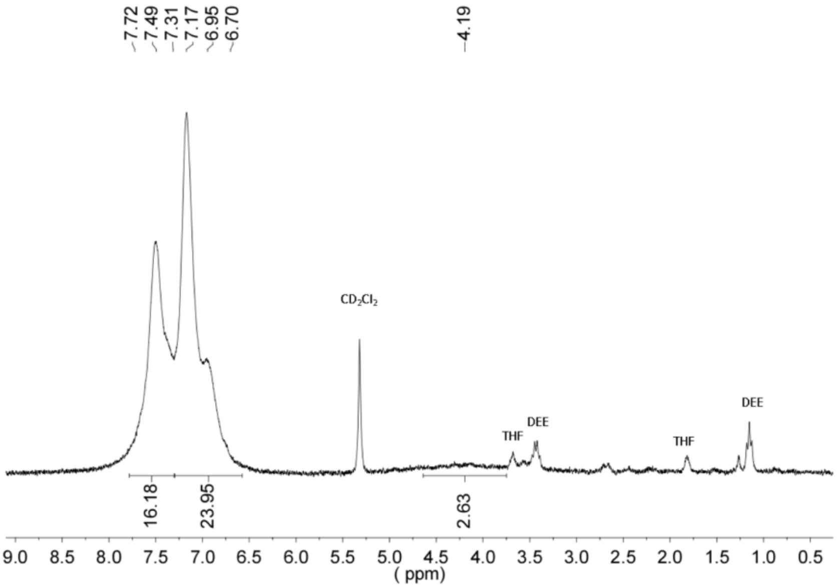


Figure S-34. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [$(CuI)_2(CDP(CH_2PPh_2)_2$] (**15**).

[$(CuSPh)_2(CDP(CH_2PPh_2)_2$] (16)

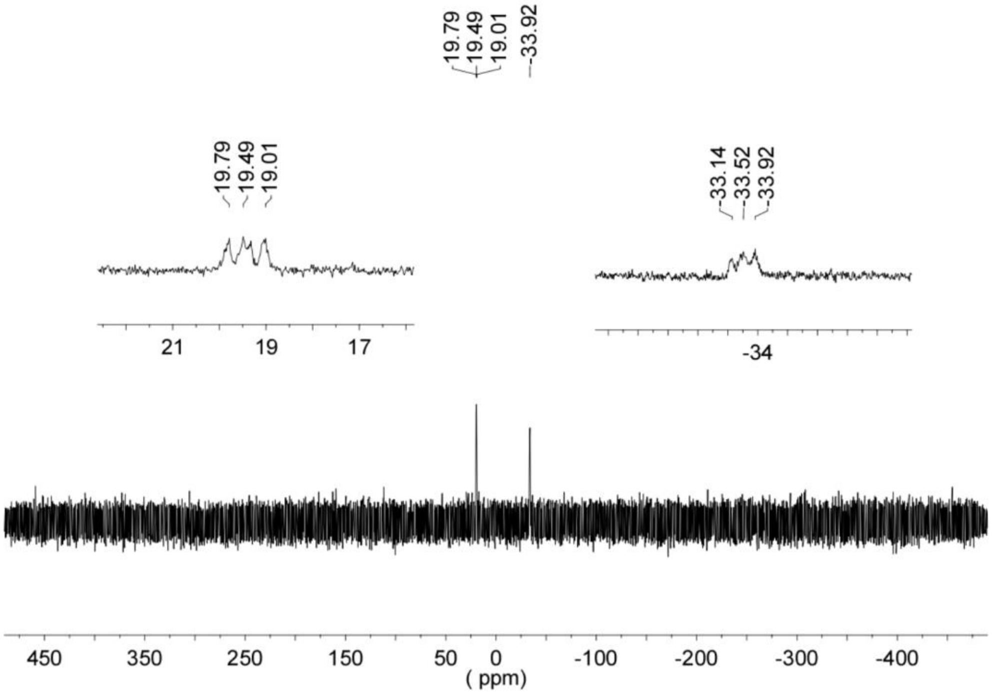


Figure S-35. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [$(CuSPh)_2(CDP(CH_2PPh_2)_2$] (**16**).

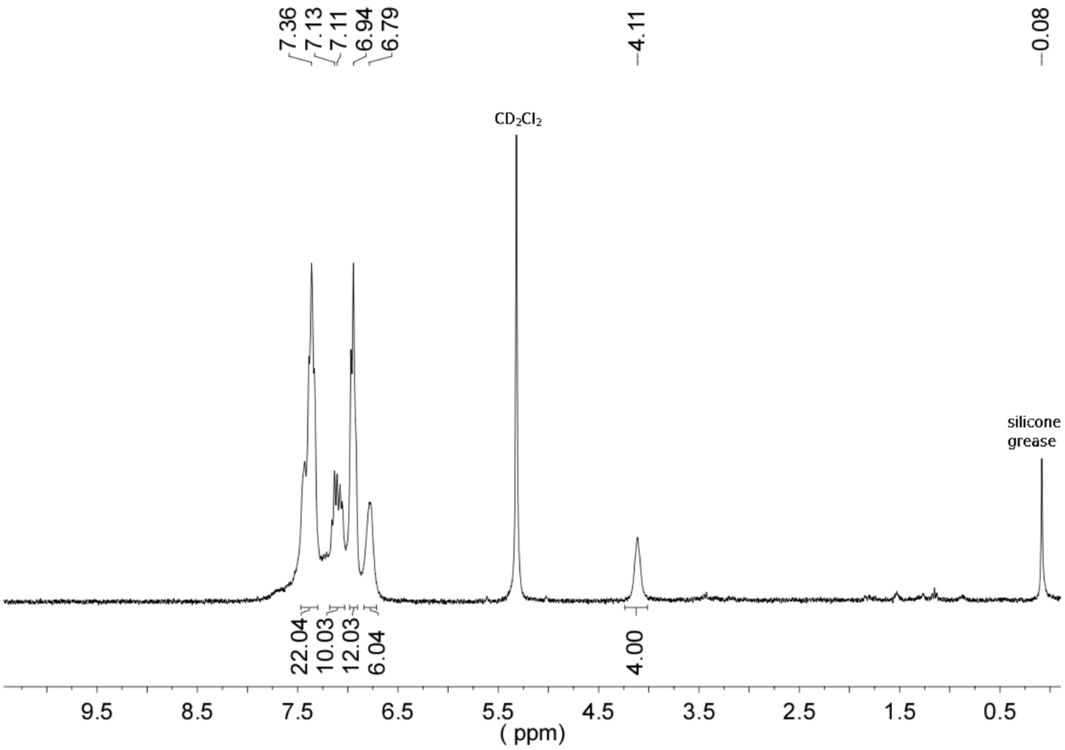


Figure S-36. ^{1}H NMR (CCl$_2$D$_2$, 300 MHz, [ppm]) of [(CuSPh)$_2$(CDP(CH$_2$PPh$_2$)$_2$] (**16**).

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

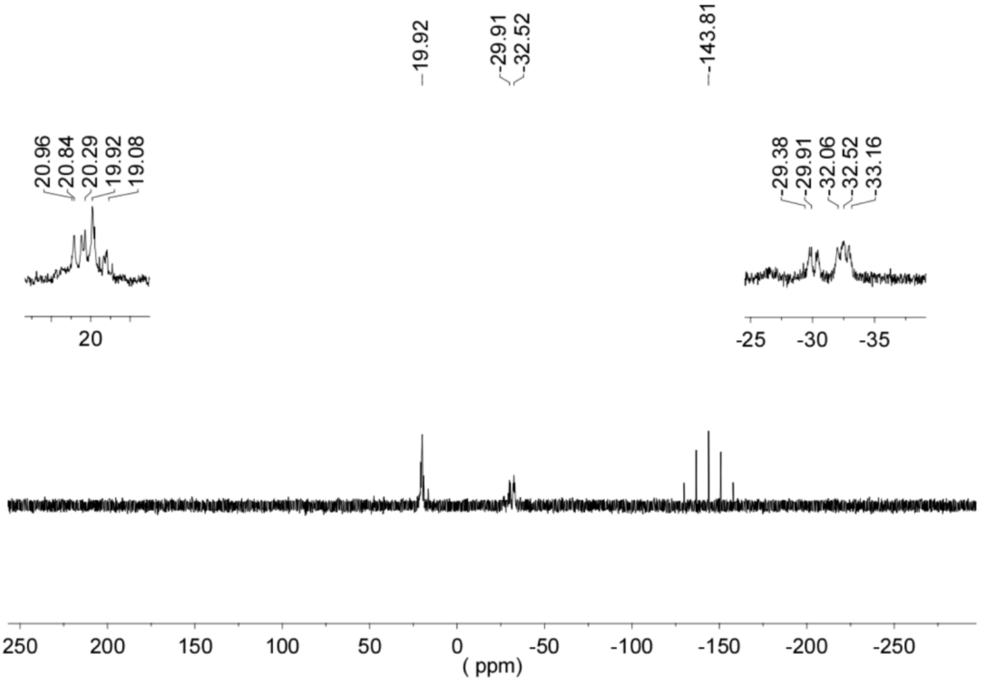


Figure S-37. ^{31}P NMR (CCl$_2$D$_2$, 101 MHz, [ppm]) of [CuCl(CDPH(CH$_2$PPh$_2$)$_2$]PF$_6$ (**17**).

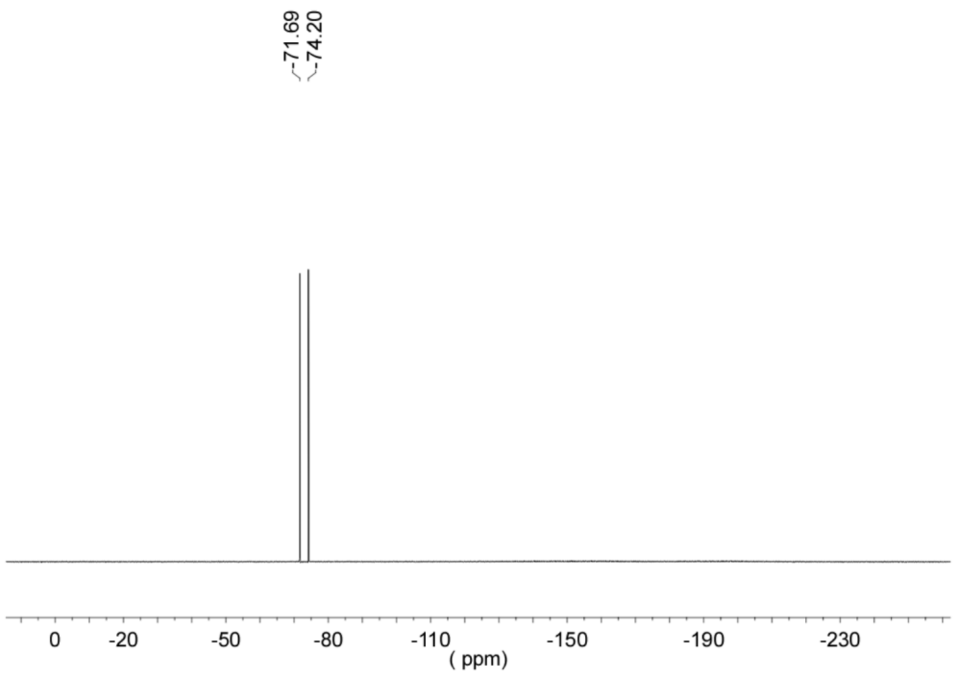


Figure S-38. ^{19}F NMR (CCl_2D_2, 282 MHz, [ppm]) of [CuCl(CDPH(CH_2PPh_2)$_2$]PF_6 (**17**).

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

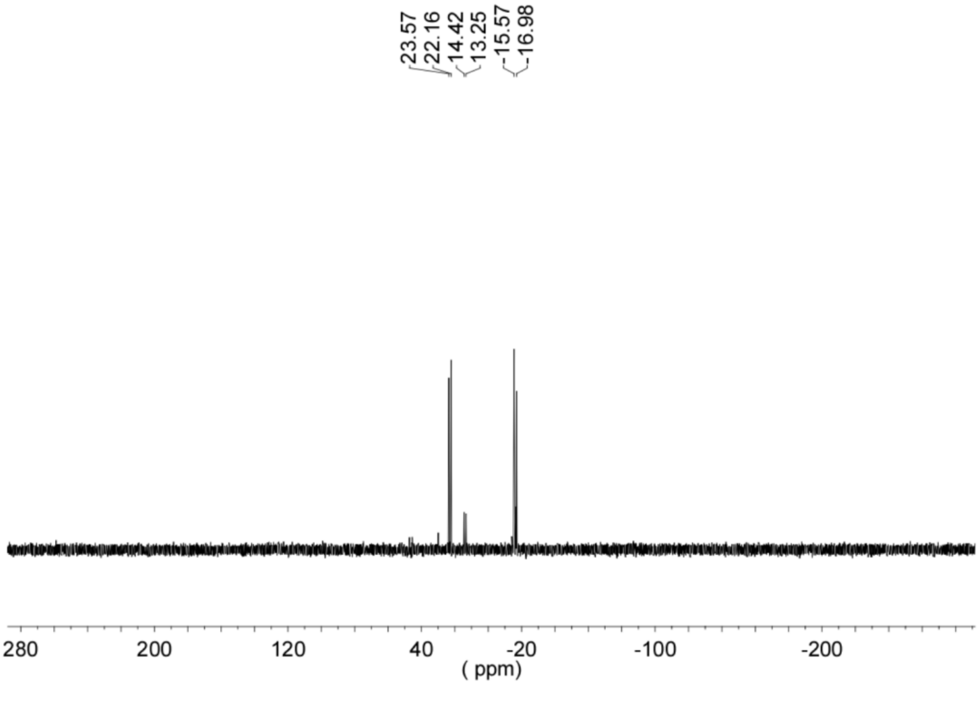


Figure S-39. ^{31}P NMR (CCl_2D_2, 101 MHz, [ppm]) of [CuPPh$_3$(CH(PPh$_2$CHPPh$_2$)$_2$] (**18**).

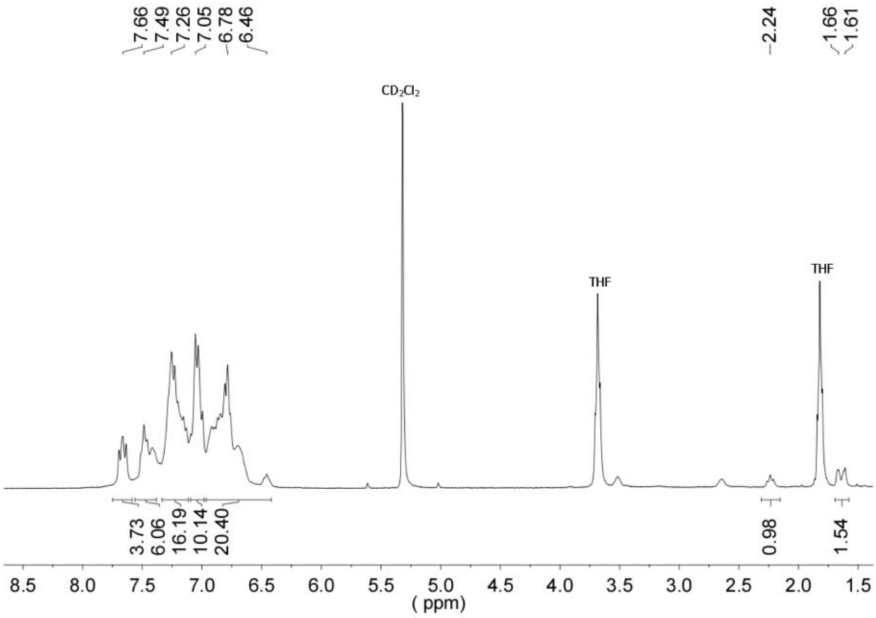


Figure S-40. ^{1}H NMR (CCl_2D_2, 300 MHz, [ppm]) of [$CuPPh_3(CH(PPh_2CHPPh_2)_2$] (**18**).

IR Spectroscopy

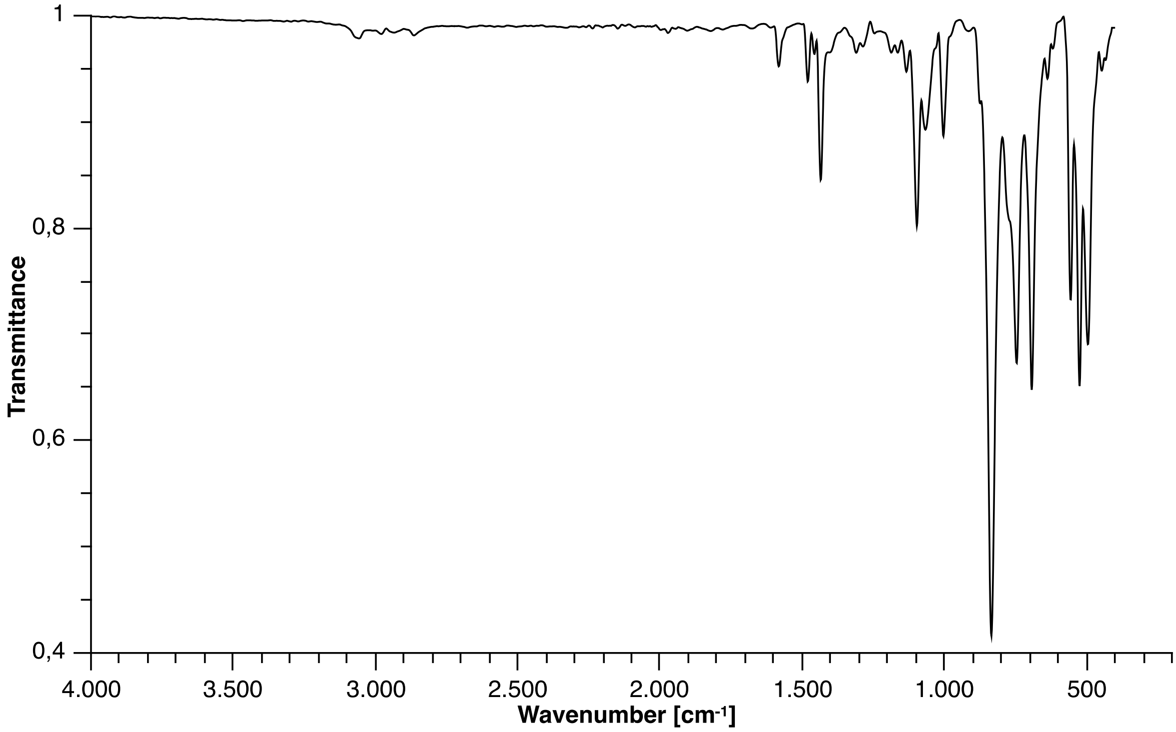
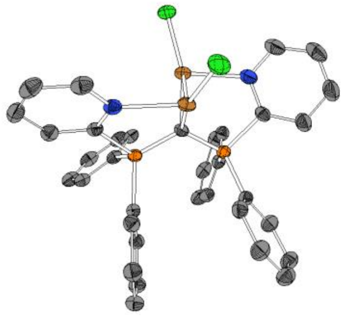


Figure S-41. Experimental IR Spectrum of $[(CuPPh_3)_2(CDP(Py)_2)](PF_6)_2$ (**4**).

Crystallographic Data

$[(CuCl)_2(CDP(Py)_2)]$ (2)

MKML27 | CCDC: 2017394



Crystal data

$C_{35}H_{28}Cl_2Cu_2N_2P_2$

Block

Yellow

Triclinic

$P\bar{1}$

Z = 4

a = 10.5074(2) Å

b = 15.9277(3) Å

c = 19.8575(4) Å

α = 82.0400(10) °

β = 80.765(2) °

γ = 80.376(2) °

V = 3212.73(11) $Å^3$

μ = 0.465 mm^{-1}

$F(000)$ = 1496

0.182 x 0.151 x 0.094 mm^3

M = 0.73651 $kg\cdot mol^{-1}$

D_{calc} = 1.523 $g\cdot cm^{-3}$

N_{ref} = 43369

Θ_{min} = 4.3 °

Θ_{max} = 75.7 °

Data collection

X-Area Pilatus3_SV 1.31.127.0 (Stoe, 2016)

λ = 1.54178 Å

Θ_{min} = 4.310 °

Θ_{max} = 66.593 °

T = 100(2) K

$h = 12 \rightarrow -7$

$k = 18 \rightarrow -18$

$l = 23 \rightarrow -23$

Structure solution / refinement

N_{ref} measured = 43764

N_{ref} independent = 11181

R_{Int} = 0.0277

Semi-empirical from equivalents

T_{max} = 0.9848;

T_{min} = 0.4528

Full-matrix least-squares on F^2

$C_{25.00\,°}$ = 98.6%

N_{ref} used = 11181

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

$\Delta\rho_{max}$ = 0.507 $eÅ^{-3}$

$\Delta\rho_{max}$ = –0.614 $eÅ^{-3}$

N_{ref} = 11181

$N_{restraints}$ = 6

$N_{parameters}$ = 795

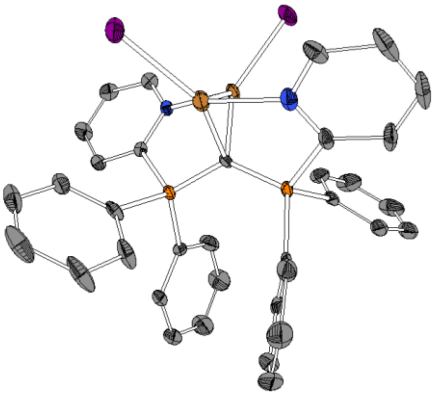
$R_1(I>2\sigma(I))$ = 0.0337

$\omega R_2(I)$ = 0.0864

$GooF(F^2)$ = 1.045

$[(CuCl)_2(CDP(Py)_2)]$ (3)

MKP80 | CCDC: 2017392



Crystal data

$C_{35}H_{28}I_2Cu_2N_2P_2$	Block	Orange
Triclinic	$P\bar{1}$	Z = 2
a = 12.0153(5) Å	b = 12.8465(5) Å	c = 13.5785(6) Å
α = 109.8360(10) °	β = 94.1550(10) °	γ = 93.9560(10) °
V = 1956.56(14) $Å^3$	μ = 2.770 mm^{-1}	$F(000)$ = 892
0.140 x 0.130 x 0.110 mm^3	M = 0.91943 kg·mol^{-1}	D_{calc} = 1.561 g·cm^{-3}
N_{ref} = 9708	Θ_{min} = 2.5 °	Θ_{max} = 26.6 °

Data collection

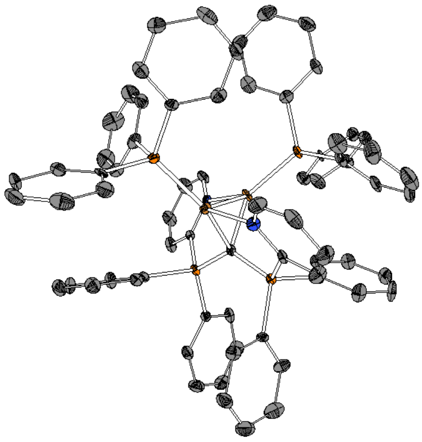
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.282 °	Θ_{max} = 25.027 °	
$h = 14 \rightarrow -14$	$k = 15 \rightarrow -15$	$l = 16 \rightarrow -15$

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
$C_{25.00\,°}$ = 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)

MKP82| CCDC: 2017399



Crystal data

$C_{151}H_{129}Cl_{18}Cu_4F_{24}N_4P_{12}$	Block	Yellow
Monoclinic	*Pn*	Z = 2
a = 16.7727(6) Å	b = 22.4945(8) Å	c = 21.1551(7) Å
α = 90 °	β = 94.708(3) °	γ = 90 °
V = 7954.8(5) $Å^3$	μ = 1.030 mm^{-1}	*F*(000) = 3762
0.722 x 0.222 x 0.198 mm^3	*M* = 3.71953 $kg \cdot mol^{-1}$	D_{calc} = 1.553 $g \cdot cm^{-3}$
N_{ref} = 9066	Θ_{min} = 2.3 °	Θ_{max} = 27.8 °

Data collection

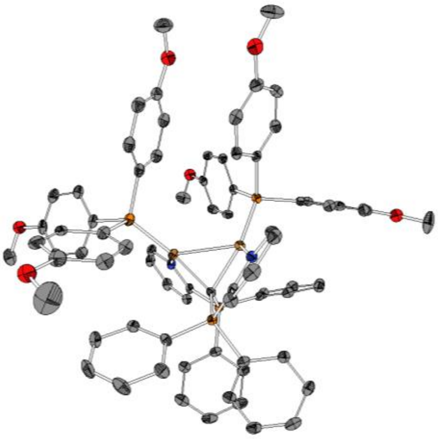
D8 Quest (Bruker AXS Inc.)	*T* = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.134 °	Θ_{max} = 25.026 °	
h = 19 → –19	*k* = 24 → –26	*l* = 25→ –25

Structure solution / refinement

N_{ref} measured = 71983	N_{ref} independent = 27071	R_{Int} = 0.0904
Semi-empirical from equivalents	T_{max} = 0.7456; T_{min} = 0.4636	Full-matrix least-squares on F^2
$C_{25.00\,°}$ = 99.9%	N_{ref} used = 27071	N_{ref} $I > 2\sigma(I)$ = 22422
$\Delta\rho_{max}$ = 0.910 $eÅ^{-3}$	$\Delta\rho_{max}$ = –0.651 $eÅ^{-3}$	
N_{ref} = 27071	$N_{restraints}$ = 972	$N_{parameters}$ = 1928
$R_1(I > 2\sigma(I))$ = 0.0609	$\omega R_2(I)$ = 0.1560	$GooF(F^2)$ = 1.035

$[(Cu(PPhOMe)_3)_2(CDP(Py)_2)](PF_6)_2$ (5)

MKND122 | CCDC: 2017397



Crystal data

$C_{182}H_{196}Cu_4F_{24}N_4O_{19}P_{12}$	Block	Yellow
Triclinic	$P2_1/n$	Z = 2
a = 18.8255(11) Å	b = 24.2698(15) Å	c = 20.5171(12) Å
α = 90 °	β = 110.359(2) °	γ = 90 °
V = 8788.5(9) $Å^3$	μ = 0.678 mm^{-1}	$F(000)$ = 884.2
0.220 x 0.181 x 0.133 mm^3	M = 3.82528 $kg{\cdot}mol^{-1}$	D_{calc} = 1.446 $g{\cdot}cm^{-3}$
N_{ref} = 99844	Θ_{min} = 2.3 °	Θ_{max} = 28.8 °

Data collection

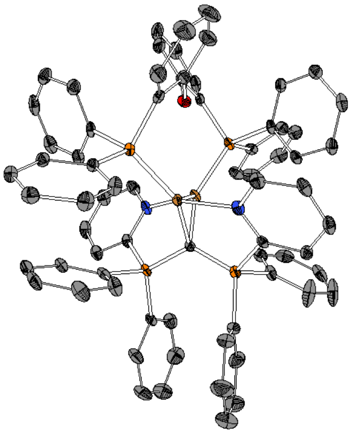
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.195 °	Θ_{max} = 25.027 °	
$h = 22 \rightarrow -22$	$k = 28 \rightarrow -28$	$l = 24 \rightarrow -24$

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
$C_{25.00\,°}$ = 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

$[Cu_2(DPEPhos)(CDP(Py)_2)](PF_6)_2$ (6)

MKND134 | CCDC: 2017398



Crystal data

$C_{73}H_{60}Cl_4Cu_2F_{12}N_2OP_6$	Block	Intense Yellow
Triclinic	$P\bar{1}$	Z = 2
a = 13.2598(8) Å	b = 13.7699(8) Å	c = 23.8017(15) Å
α =87.929(2) °	β = 78.411(2) °	γ = 68.542(2) °
V = 3958.9(4) $Å^3$	μ = 0.864 mm^{-1}	$F(000)$ = 1688
0.520 x 0.216 x 0.199 mm^3	M = 1.66395 kg·mol^{-1}	D_{calc} = 1.396 g·cm^{-3}
N_{ref} = 9851	Θ_{min} = 2.6 °	Θ_{max} = 29.1 °

Data collection

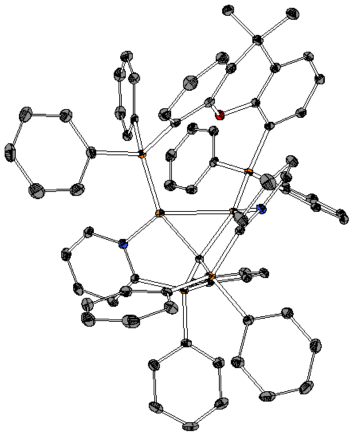
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.156 °	Θ_{max} = 25.027 °	
$h = 15 \rightarrow -15$	$k = 16 \rightarrow -16$	$l = 28 \rightarrow -28$

Structure solution / refinement

N_{ref} measured = 81101	N_{ref} independent = 13988	R_{Int} = 0.0466
Semi-empirical from equivalents	T_{max} = 0.7458 T_{min} = 0.6532	Full-matrix least-squares on F^2
$C_{25.00\,°}$ = 99.9%	N_{ref} used = 13988	N_{ref} $I>2\sigma(I)$ = 5608
$\Delta\rho_{max}$ = 0.525 e$Å^{-3}$	$\Delta\rho_{max}$ = –0.708 e$Å^{-3}$	
N_{ref} = 13988	$N_{restraints}$ = 24	$N_{parameters}$ = 908
$R_1(I>2\sigma(I))$ = 0.0510	$\omega R_2(I)$ = 0.1166	$GooF(F^2)$ = 1.076

[Cu_2(XantPhos)(CDP(Py)$_2$)](PF_6)$_2$ (7)

MKPM123 | CCDC: 2017400



Crystal data

$C_{76}H_{64}Cl_4Cu_2F_{12}N_2OP_6$	Block	Fluorescent Yellow
Triclinic	$P\overline{1}$	Z = 2
a = 12.7458(6) Å	b = 13.1266(6) Å	c = 21.8612(11) Å
α = 87.898(2) °	β = 83.248(2) °	γ = 83.122(2) °
V = 3605.1(3) Å^3	μ = 0.951 mm^{-1}	$F(000)$ = 1732
0.324 x 0.267 x 0.172 mm^3	M = 1.70402 kg·mol^{-1}	D_{calc} = 1.570 g·cm^{-3}
N_{ref} = 9459	Θ_{min} = 2.3 °	Θ_{max} = 29.2 °

Data collection

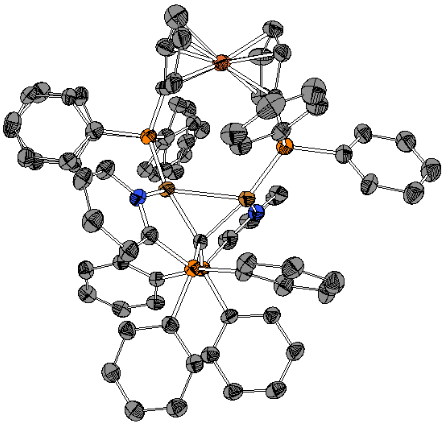
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.116 °	Θ_{max} = 25.027 °	
$h = 15 \rightarrow -15$	$k = 15 \rightarrow -15$	$l = 26 \rightarrow -26$

Structure solution / refinement

N_{ref} measured = 80679	N_{ref} independent = 12680	R_{Int} = 0.0270
Semi-empirical from equivalents	T_{max} = 0.7458; T_{min} = 0.6926	Full-matrix least-squares on F^2
$C_{25.00\,°}$ = 99.6%	N_{ref} used = 12680	N_{ref} $I>2\sigma(I)$ = 11570
$\Delta\rho_{max}$ = 0.735 eÅ^{-3}	$\Delta\rho_{max}$ = –0.496 eÅ^{-3}	
N_{ref} = 12680	$N_{restraints}$ = 0	$N_{parameters}$ = 930
$R_1(I>2\sigma(I))$ = 0.0276	$\omega R_2(I)$ = 0.0718	$GooF(F^2)$ = 1.023

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

MKPM124 | CCDC: 2017406



Crystal data

$C_{72}H_{62}Cl_6Cu_2F_{12}FeN_2P_6$ Block Yellow

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

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

α = 85.242(2) ° β = 81.225(2) ° γ = 67.120(2) °

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

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

N_{ref} = 27362 Θ_{min} = 3.7 ° Θ_{max} = 75.6 °

Data collection

X-Area Pilatus3_SV 1.31.127.0 (Stoe, 2016) λ = 1.54178 Å

Θ_{min} = 3.667 ° Θ_{max} = 66.595 ° T = 100(2) K

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

Structure solution / refinement

N_{ref} measured = 65269 N_{ref} independent = 13098 R_{Int} = 0.0734

Semi-empirical from equivalents T_{max} = 0.9498; T_{min} = 0.2242 Full-matrix least-squares on F^2

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

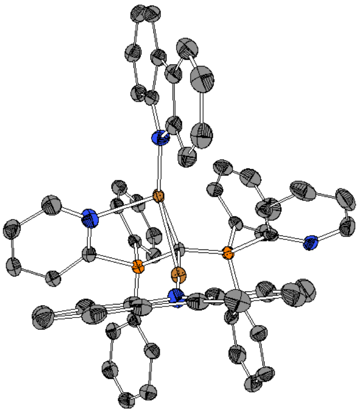
$\Delta\rho_{max}$ = 3.149 eÅ^{-3} $\Delta\rho_{max}$ = –1.060 eÅ^{-3}

N_{ref} = 13098 $N_{restraints}$ = 100 $N_{parameters}$ = 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

$C_{61}H_{48}Cl_4Cu_2N_4P_2$	Block	Yellow
Monoclinic	$P2_1/n$	Z = 4
a =12.9899(2) Å	b = 26.8839(4) Å	c = 16.5110(2) Å
α = 90 °	β = 111.9520(10) °	γ = 90 °
V = 5347.91(14) Å^3	μ = 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	Θ_{min} = 3.3°	Θ_{max} = 76.1 °

Data collection

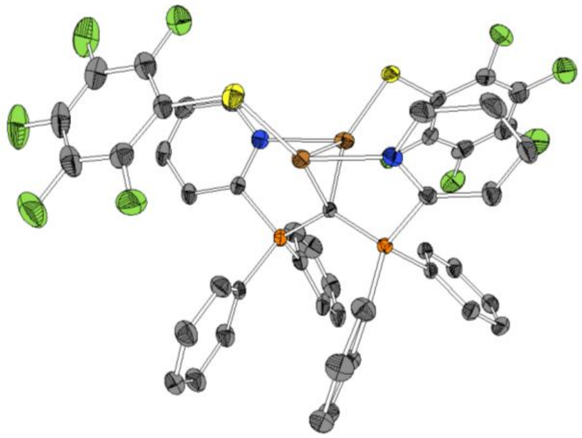
X-Area Pilatus3_SV 1.31.127.0 (Stoe, 2016)		λ = 1.54178 Å
Θ_{min} = 3.725 °	Θ_{max} = 66.590 °	T = 100(2) K
$h = 15 \rightarrow -15$	$k = 32 \rightarrow -19$	$l = 19 \rightarrow -19$

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

$[(\mathrm{CuS(C_6F_5)})_2(\mathrm{CDP(Py)_2})]$ (9)

MKMN26 | CCDC: 2017395



Crystal data

$C_{47}H_{28}Cu_2F_{10}N_2P_2S_2$

Needle

Orange

Triclinic

$P\overline{1}$

Z = 2

a = 10.295(2) Å

b = 13.312(3) Å

c = 16.579(3) Å

α = 71.143(5) °

β = 85.319(6) °

γ = 80.351(6) °

V = 2118.8(8) Å^3

μ = 1.261 mm^{-1}

$F(000)$ = 4032

0.358 x 0.117 x 0.056 mm^3

M = 1.06385 kg·mol^{-1}

D_{calc} = 1.667 g·cm^{-3}

N_{ref} = 9758

Θ_{min} = 2.4°

Θ_{max} = 28.5 °

Data collection

D8 Quest (Bruker AXS Inc.)

T = 100(2) K

λ = 0.71073 Å

Θ_{min} = 2.359 °

Θ_{max} = 29.161 °

$h = 14 \rightarrow -14$

$k = 18 \rightarrow -18$

$l = 22 \rightarrow -20$

Structure solution / refinement

N_{ref} measured = 69728

N_{ref} independent = 11371

R_{Int} = 0.0698

Semi-empirical from equivalents

T_{max} = 0.7458;

T_{min} = 0.6599

Full-matrix least-squares on F^2

$C_{25.00\,^\circ}$ = 99.9%

N_{ref} used = 11371

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

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

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

N_{ref} = 11371

$N_{\mathrm{restraints}}$ = 0

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

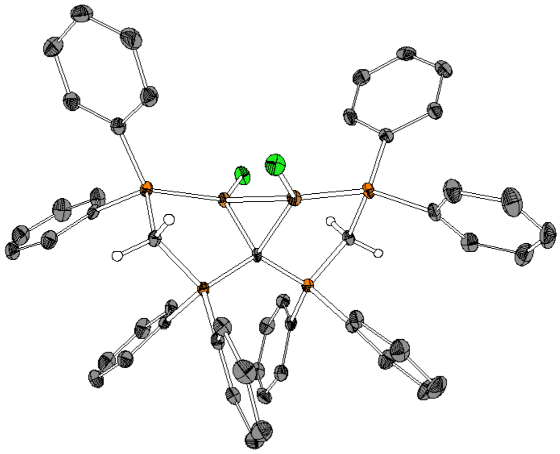
$R_1(I>2\sigma(I))$ = 0.0527

$\omega R_2(I)$ = 0.1115

$GooF(F^2)$ = 1.028

$[(CuCl)_2(CDP(CH_2PPh_2)_2]$ (14)

MKMW30 | CCDC: 2017408



Crystal data

$C_{55}H_{52}Cl_{10}Cu_2P_4$	Block	Clear Colourless
Triclinic	$P\bar{1}$	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) $Å^3$	μ = 1.344 mm^{-1}	$F(000)$ = 1340
0.560 x 0.390 x 0.240 mm^3	M = 1.31845 $kg{\cdot}mol^{-1}$	D_{calc} = 1.513 $g{\cdot}cm^{-3}$
N_{ref} = 9305	Θ_{min} = 2.4 °	Θ_{max} = 29.2 °

Data collection

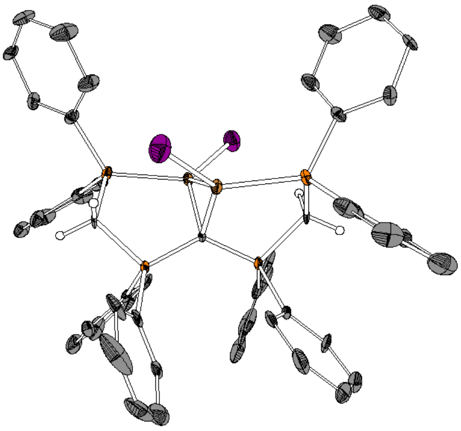
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.293 °	Θ_{max} = 25.027 °	
$h = 14 \rightarrow -14$	$k = 15 \rightarrow -15$	$l = 23 \rightarrow -23$

Structure solution / refinement

N_{ref} measured = 64909	N_{ref} independent = 10222	R_{Int} = 0.0377
Semi-empirical from equivalents	T_{max} = 0.7458; T_{min} = 0.6081	Full-matrix least-squares on F^2
$C_{25.00\,°}$ = 99.9%	N_{ref} used = 10222	N_{ref} $I>2\sigma(I)$ = 8783
$\Delta\rho_{max}$ = 0.439 $eÅ^{-3}$	$\Delta\rho_{max}$ = –0.635 $eÅ^{-3}$	
N_{ref} = 10222	$N_{restraints}$ = 6	$N_{parameters}$ = 695
$R_1(I>2\sigma(I))$ = 0.0314	$\omega R_2(I)$ = 0.0736	$GooF(F^2)$ = 1.056

$[(\mathrm{CuI})_2(\mathrm{CDP}(\mathrm{CH_2PPh_2})_2)]$ (15)

MKCR5 | CCDC: 2017410



Crystal data

$C_{51}H_{44}Cu_2I_2P_4$

Block

Translucent Yellow

Monoclinic

$C2/c$

Z = 4

a = 15.1057(8) Å

b = 17.1264(9) Å

c = 20.0035(11) Å

α = 90 °

β = 93.099(2) °

γ = 90 °

V = 5167.5(5) $Å^3$

μ = 2.173 mm^{-1}

$F(000)$ = 2296

0.440 x 0.286 x 0.231 mm^3

M = 1.16162 kg·mol^{-1}

D_{calc} = 1.4923g·cm^{-3}

N_{ref} = 9712

Θ_{min} = 2.4 °

Θ_{max} = 28.5 °

Data collection

D8 Quest (Bruker AXS Inc.)

T = 100(2) K

λ = 0.71073 Å

Θ_{min} = 2.104 °

Θ_{max} = 29.272 °

$h = 20 \rightarrow -19$

$k = 23 \rightarrow -23$

$l = 26 \rightarrow -26$

Structure solution / refinement

N_{ref} measured = 82870

N_{ref} independent = 6967

R_{Int} = 0.0740

Semi-empirical from equivalents

T_{max} = 0.7458;

T_{min} = 0.6741

Full-matrix least-squares on F^2

$C_{25.00\,^\circ}$ = 99.9%

N_{ref} used = 6967

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

$\Delta\rho_{max}$ = 2.286 $eÅ^{-3}$

$\Delta\rho_{max}$ = –2.211 $eÅ^{-3}$

N_{ref} = 6967

$N_{restraints}$ = 12

$N_{parameters}$ = 268

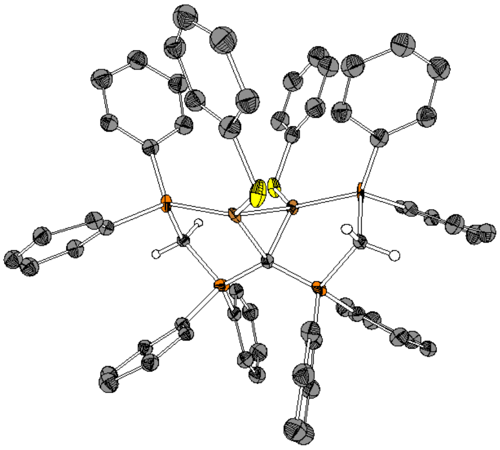
$R_1(I>2\sigma(I))$ = 0.0603

$\omega R_2(I)$ = 0.1889

$GooF(F^2)$ = 1.043

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

MKP199 | CCDC: 2017409



Crystal data

$C_{138}H_{132}Cu_4O_3P_8S_4$	Needle	Fluorescent Yellow
Triclinic	$P\bar{1}$	Z = 2
a = 16.3134(17) Å	b = 20.256(2) Å	c = 20.393(2) Å
α = 63.399(3) °	β = 84.454(3) °	γ = 86.908(3) °
V = 5996.6(11) Å^3	μ = 0.930 mm^{-1}	$F(000)$ = 2568
0.693 x 0.179 x 0.098 mm^3	M = 2.46864 kg·mol^{-1}	D_{calc} = 1.367 g·cm^{-3}
N_{ref} = 7286	Θ_{min} = 2.2 °	Θ_{max} = 23.9 °

Data collection

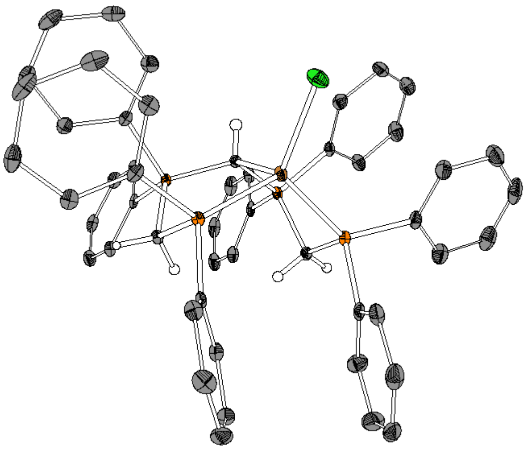
D8 Quest (Bruker AXS Inc.)	T = 100(2) K	λ = 0.71073 Å
Θ_{min} = 2.241 °	Θ_{max} = 25.027 °	
$h = 19 \rightarrow -19$	$k = 21 \rightarrow -24$	$l = 24 \rightarrow 0$

Structure solution / refinement

N_{ref} measured = 21786	N_{ref} independent = 21786	R_{Int} = 0.00
Semi-empirical from equivalents	T_{max} = 0.205084; T_{min} = 0.161605	Full-matrix least-squares on F^2
$C_{25.00\,°}$ = 99.7%	N_{ref} used = 21786	N_{ref} $I>2\sigma(I)$ = 12003
$\Delta\rho_{max}$ = 0.994 eÅ^{-3}	$\Delta\rho_{max}$ = –0.940 eÅ^{-3}	
N_{ref} = 21786	$N_{restraints}$ = 2036	$N_{parameters}$ = 1415
$R_1(I>2\sigma(I))$ = 0.1125	$\omega R_2(I)$ = 0.1874	$GooF(F^2)$ = 1.050

$\mathrm{[CuCl(CDPH(CH_2PPh_2)_2]PF_6}$ (17)

MKP42 | CCDC: 2017407



Crystal data

$\mathrm{C_{52}H_{47}Cl_3CuF_6P_5}$
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) Å^3
μ = 0.801 mm^{-1}
F(000) = 4544

0.440 x 0.221 x 0.186 mm^3
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 F^2

$C_{25.00\,°}$ = 99.9%
N_{ref} used = 8988
N_{ref} $I>2\sigma(I)$ = 7804

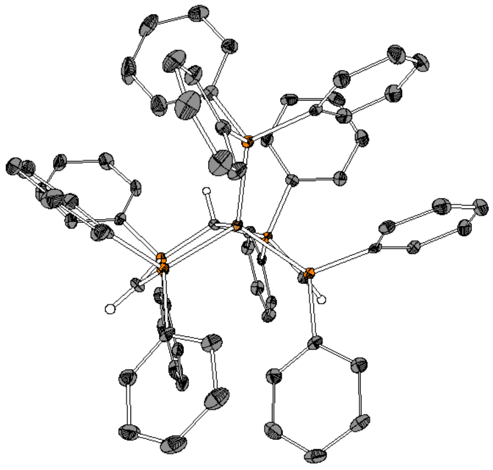
$\Delta\rho_{\mathrm{max}}$ = 0.748 eÅ^{-3}
$\Delta\rho_{\mathrm{max}}$ = –0.941 eÅ^{-3}

N_{ref} = 8988
$N_{\mathrm{restraints}}$ = 0
$N_{\mathrm{parameters}}$ = 625

$R_1(I>2\sigma(I))$ = 0.0332
$\omega R_2(I)$ = 0.0755
$GooF(F^2)$ = 1.050

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

MKPCR28 | CCDC: 2017411



Crystal data

$C_{73}H_{66}CuOP_5$

Block

Yellow

Monoclinic

$P2_1/c$

Z = 4

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) Å^3

μ = 0.548 mm^{-1}

$F(000)$ = 2464

0.440 x 0.221 x 0.186 mm^3

M = 1.17764 kg·mol^{-1}

D_{calc} = 1.492 g·cm^{-3}

N_{ref} = 9982

Θ_{min} = 2.4 °

Θ_{max} = 28.7 °

Data collection

D8 Quest (Bruker AXS Inc.)

T = 100(2) K

λ = 0.71073 Å

Θ_{min} = 2.065 °

Θ_{max} = 25.025 °

$h = 18 \rightarrow -18$

$k = 18 \rightarrow -18$

$l = 28 \rightarrow -28$

Structure solution / refinement

N_{ref} measured = 104671

N_{ref} independent = 10497

R_{Int} = 0.0679

Semi-empirical from equivalents

T_{max} = 0.7458;

T_{min} = 0.6758

Full-matrix least-squares on F^2

$C_{25.00\,°}$ = 99.9%

N_{ref} used = 10497

N_{ref} $I>2\sigma(I)$ = 8931

$\Delta\rho_{max}$ = 0.838 eÅ^{-3}

$\Delta\rho_{max}$ = –0.424 eÅ^{-3}

N_{ref} = 10497

$N_{restraints}$ = 0

$N_{parameters}$ = 721

$R_1(I>2\sigma(I))$ = 0.0471

$\omega R_2(I)$ = 0.1098

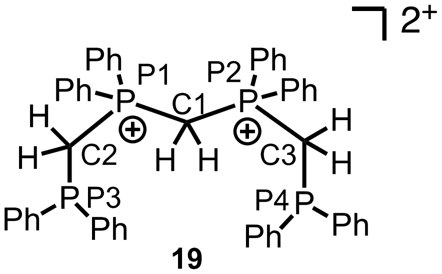
$GooF(F^2)$ = 1.164

Chemical calculations

Density functional theory (DFT) using the PBE[8,9] functional was performed to complex **8** and **10**. The def2-TZVPP[10–12] basis set was used, employing the resolution-of-identity approximation.[13–16] Further, D3-dispersion correction[17] was considered applying the Becke-Johnson damping.[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.[22]

Deprotonation of 19

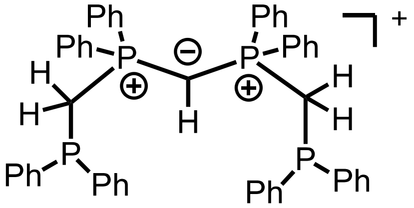
Table 1 Atomic partial charges *q*(C) of **19** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



19

	q(C)
C1	-1.10401
C2	-1.09837
C3	-1.09833
P1	1.67805
P2	1.67807
P3	0.83356
P4	0.83358
Sum =	1.72255

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

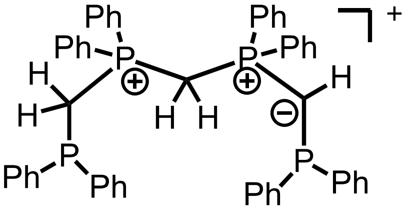


12a

	q(C)
C1	-1.39295
C2	-1.08756
C3	-1.08921
P1	1.67469
P2	1.66442

P3	0.82549
P4	0.82719
Sum =	1.42207

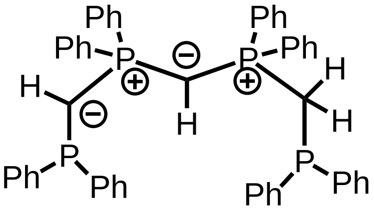
Table 3 Atomic partial charges *q*(C) of **12b** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



12b

	q(C)
C1	-1.10903
C2	-1.11819
C3	-1.34607
P1	1.69060
P2	1.66433
P3	0.82873
P4	0.82147
Sum =	1.43184

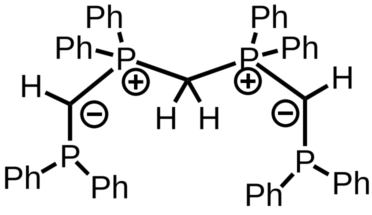
Table 4 Atomic partial charges *q*(C) of **13a** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



13a

	q(C)
C1	-1.38484
C2	-1.35280
C3	-1.10428
P1	1.66372
P2	1.68057
P3	0.81241
P4	0.80365
Sum =	1.11843

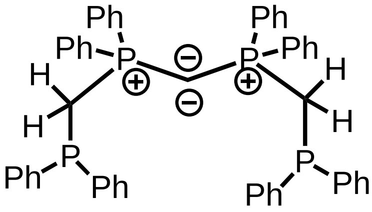
Table 5 Atomic partial charges *q*(C) of **13b** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



13b

	q(C)
C1	-1.07747
C2	-1.34641
C3	-1.34810
P1	1.66134
P2	1.66292
P3	0.82119
P4	0.82274
Sum =	1.19621

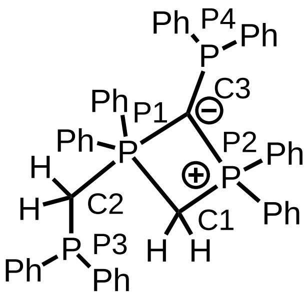
Table 6 Atomic partial charges *q*(C) of **13c** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



13c

	q(C)
C1	-1.45006
C2	-1.09378
C3	-1.09380
P1	1.61564
P2	1.61565
P3	0.81602
P4	0.81602
Sum =	1. 22569

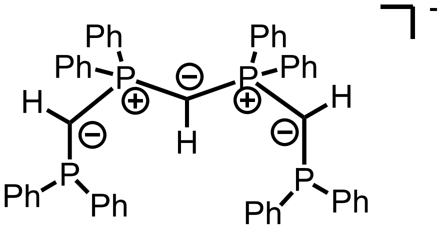
Table 7 Atomic partial charges *q*(C) of **13d** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



13d

	q(C)
C1	-1.04315
C2	-1.06590
C3	-1.38125
P1	1.58938
P2	1.58578
P3	0.82062
P4	0.79698
Sum =	1.30246

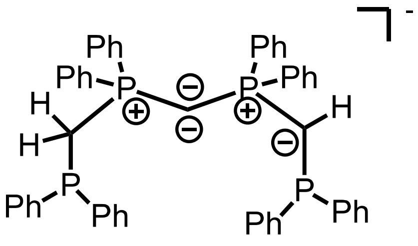
Table 8 Atomic partial charges *q*(C) of **20a** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



20a

	q(C)
C1	-1.38576
C2	-1.37257
C3	-1.37253
P1	1.67775
P2	1.67769
P3	0.83322
P4	0.83321
Sum =	0.89101

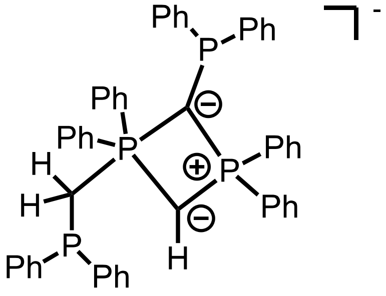
Table 8 Atomic partial charges *q*(C) of **20b** calculated by the NBO method at the PBE-D3(BJ)/def2-TZVPP level of theory.



20b

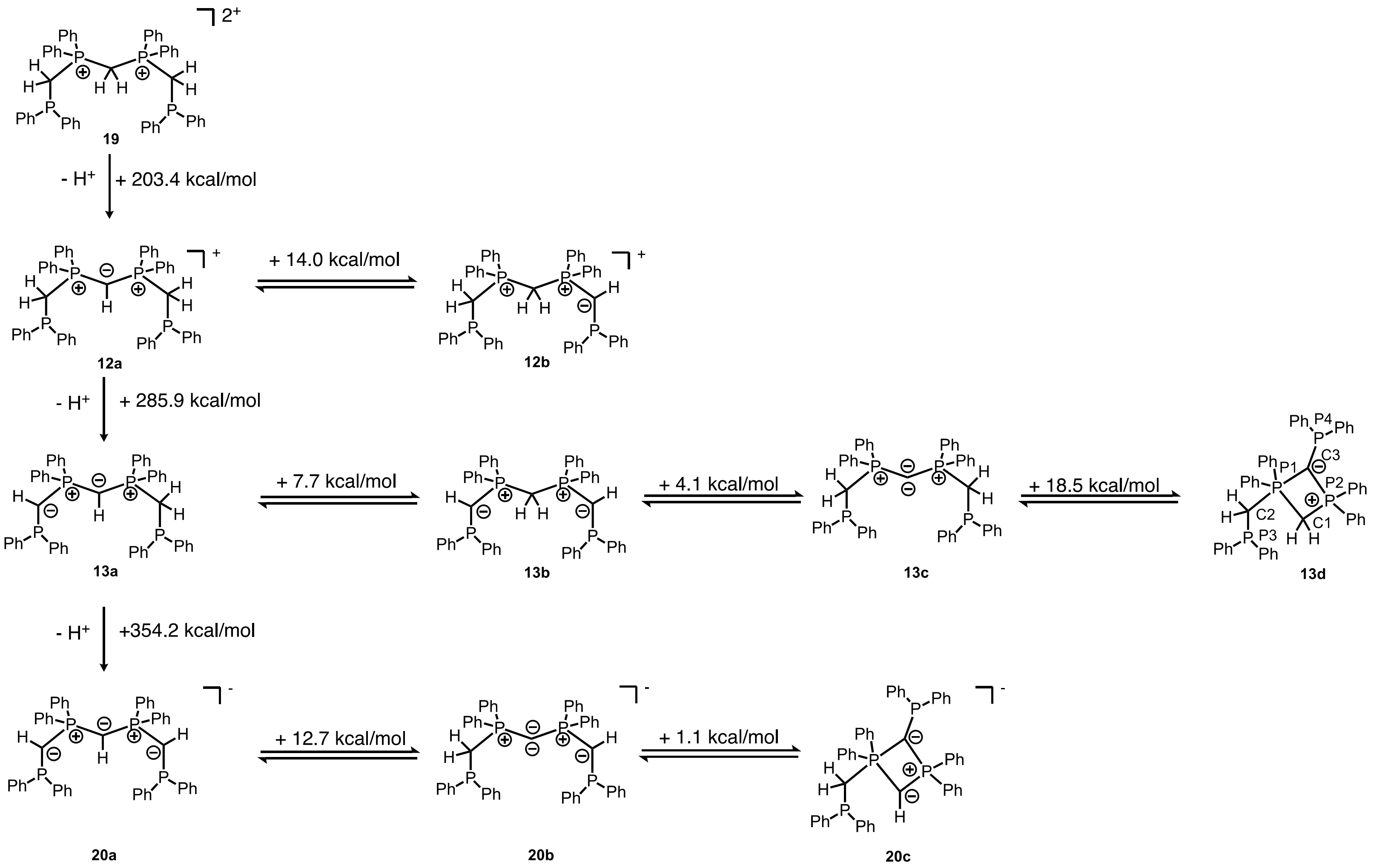
	q(C)
C1	-1.49850
C2	-1.11141
C3	-1.36223
P1	1.59666
P2	1.64607
P3	0.82008
P4	0.82936
Sum =	0.92003

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



20c

	q(C)
C1	-1.31933
C2	-1.06983
C3	-1.41583
P1	1.58006
P2	1.60939
P3	0.83700
P4	0.84920
Sum =	1.07066



Scheme S-1. Calculation of the stepwise deprotonation of [CH$_2$(PPh$_2$CHPPh$_2$)$_2$]Cl$_2$ (**19**). Stable tautomers are shown with their corresponding energy difference in kcal/mol. The positive value of the engery 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.

Kohn-Sham orbitals

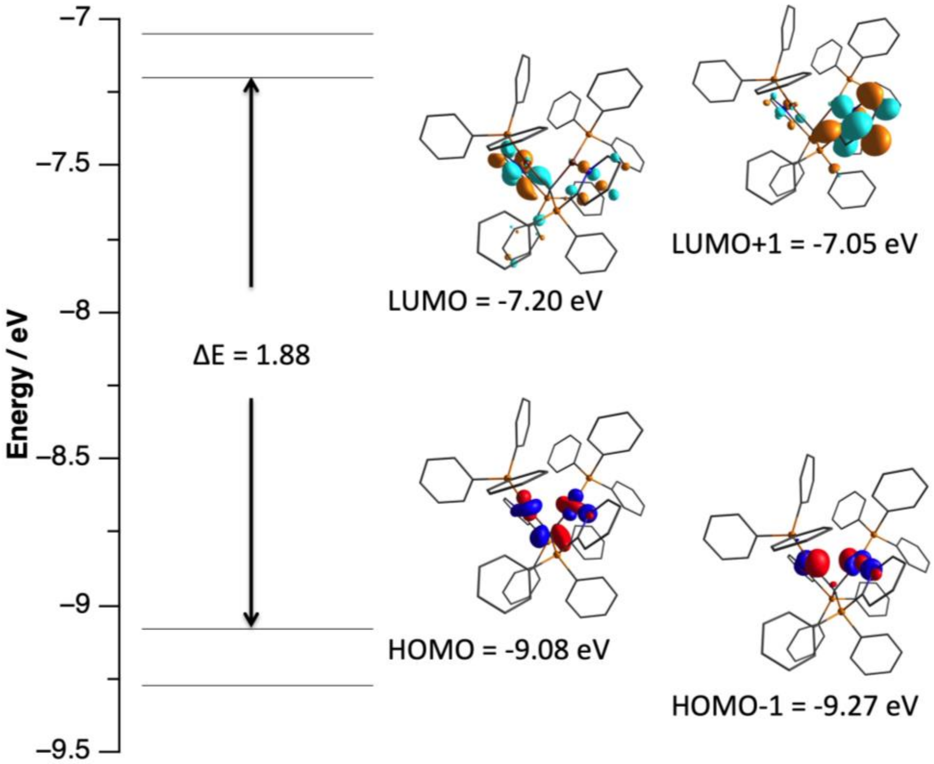


Figure S-42. Kohn-Sham orbitals of HOMO-1, HOMO, LUMO and LUMO+1 for $[(CuCl)_2(CDP(CH_2PPh_2)_2]$ (**14**)calculated for the optimized gas phase S_0 state geometry (isovalue = 0.05). Calculations were performed at the PBE-D3(BJ)/def2-TZVPP level of theory.

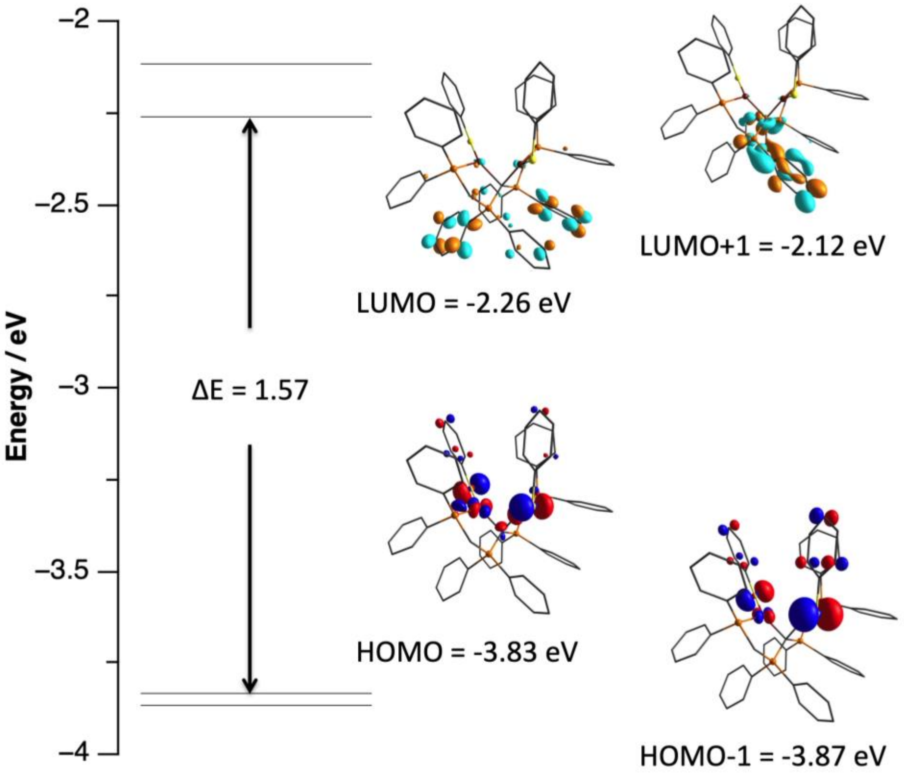


Figure S-43. Kohn-Sham orbitals of HOMO-1, HOMO, LUMO and LUMO+1 for $[(CuSPh)_2(CDP(CH_2PPh_2)_2]$ (**16**) calculated for the optimized gas phase S_0 state geometry (isovalue = 0.05). Calculations were performed at the PBE-D3(BJ)/def2-TZVPP level of theory.

Atomic coordinates

For Atomic coordinates see the XYZ file.

Literature

(1) Armarego, W. L. F.; Perin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, Aucklnad, Boston, Johannesburg, Melbourne, New Delhi, 1996.

(2) Klein, M.; Xie, X.; Burghaus, O.; Sundermeyer, J. Synthesis and Characterization of a N,C,N-Carbodiphosphorane Pincer Ligand and Its Complexes. *Organometallics* **2019**.

(3) Stallinger, S.; Reitsamer, C.; Schuh, W.; Kopacka, H.; Wurst, K.; Peringer, P. Novel Route to Carbodiphosphoranes Producing a New P,C,P Pincer Carbene Ligand. *Chem. Commun.* **2007**, No. 5, 510–512.

(4) Reitsamer, C.; Stallinger, S.; Schuh, W.; Kopacka, H.; Wurst, K.; Obendorf, D.; Peringer, P. Novel Access to Carbodiphosphoranes in the Coordination Sphere of Group 10 Metals: Template Synthesis and Protonation of PCP Pincer Carbodiphosphorane Complexes of C(Dppm)2. *Dalt. Trans.* **2012**, *41* (12), 3503–3514.

(5) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.

(6) Williams, D. B. G.; Lawton, M. Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants. *J. Org. Chem.* **2010**, *75* (24), 8351–8354.

(7) Reitsamer, C.; Schuh, W.; Kopacka, H.; Wurst, K.; Peringer, P. Synthesis and Structure of the First Heterodinuclear PCP−Pincer−CDP Complex with a Pd−Au D8−d10 Pseudo-Closed-Shell Interaction. *Organometallics* **2009**, *28* (22), 6617–6620.

(8) Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Errata: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, *78* (7), 1396.

(10) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets of Triple Zeta Valence Quality for Atoms Li to Kr. *J. Chem. Phys.* **1994**, *100* (8), 5829–5835.

(11) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence{,} Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297–3305.

(12) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057–1065.

(13) Weigend, F. A Fully Direct RI-HF Algorithm: Implementation, Optimised Auxiliary Basis Sets, Demonstration of Accuracy and Efficiency. *Phys. Chem. Chem. Phys.* **2002**, *4* (18), 4285–4291.

(14) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Auxiliary Basis Sets to Approximate Coulomb Potentials. *Chem. Phys. Lett.* **1995**, *240* (4), 283–290.

(15) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Auxiliary Basis Sets for Main Row Atoms and Transition Metals and Their Use to Approximate Coulomb Potentials. *Theor. Chem. Acc.* **1997**, *97* (1–4), 119–124.

(16) Von Arnim, M.; Ahlrichs, R. Performance of Parallel TURBOMOLE for Density Functional Calculations. *J. Comput. Chem.* **1998**, *19* (15), 1746–1757.

(17) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104–154119.

(18) Becke, A. D.; Johnson, E. R. A Density-Functional Model of the Dispersion Interaction. *J. Chem. Phys.* **2005**, *123* (15), 154101–154109.

(19) Johnson, E. R.; Becke, A. D. A Post-Hartree-Fock Model of Intermolecular Interactions. *J. Chem. Phys.* **2005**, *123* (2), 24101–24107.

(20) Johnson, E. R.; Becke, A. D. A Post-Hartree-Fock Model of Intermolecular Interactions: Inclusion of Higher-Order Corrections. *J. Chem. Phys.* **2006**, *124* (17), 174104–174109.

(21) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465.

(22) Neese, F. The ORCA Program System. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *2* (1), 73–78.