Electronic Supplementary Information (ESI)

Simple and versatile selective synthesis of neutral and cationic copper(I) N-heterocyclic carbene complexes using an electrochemical procedure

Benjamin R. M. Lake,[a] Emma K. Bullough,[a] Thomas J. Williams,[b] Adrian C. Whitwood,[b] Marc A. Little[a] and Charlotte E. Willans*[a]

[a]*School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, U.K.*
[b]*Department of Chemistry, University of York, Heslington, York, YO10 5DD.*
E-mail: c.e.willans@leeds.ac.uk

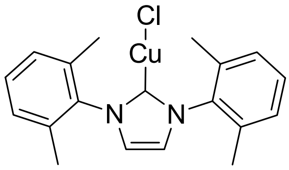
Contents

1. Experimental data

General considerations

All reagents were used as supplied or prepared as outlined without need for further purification. Ligand precursors were prepared according to literature procedure and fully characterised using NMR spectroscopy and mass spectrometry.[1-4] Manipulations were performed using standard Schlenk line and vacuum line techniques. Ar and N_2 were passed through a twin-column drying apparatus containing molecular sieves (4Å) and phosphorus pentoxide. Solvents were passed over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water via the Dow-Grubbs solvent system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (operating frequency 300.1 MHz for ^{1}H and 75.48 MHz for ^{13}C) or on a Bruker DRX500 spectrometer (operating frequency 500.13 MHz for ^{1}H and 125.80 MHz for ^{13}C). All spectra were recorded at 298K in deuterated solvent. Chemical shift values are quoted in parts per million (ppm, δ) and coupling constants J are quoted in Hertz (Hz). Assignment of ^{1}H NMR spectra was aided by the use of 2D ^{1}H^{1}H COSY experiments and the assignment of ^{13}C{^{1}H} NMR spectra was aided by ^{13}C{^{1}H} dept 135 experiments. Microanalyses were performed by Mr. Ian Blakeley in the University of Leeds, School of Chemistry. Mass spectra were collected by Ms. Tanya Marinko-Covell on a Bruker Daltonics (micro T.O.F.) instrument operating in the electrospray mode using methanol or acetonitrile as solvent.

[1,3-Bis(2,6-dimethylphenyl)imidazolin-2-ylidene]copper(I)chloride (1c)



1a (0.30 g, 0.97 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (10 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The potential across the electrodes was adjusted so that a current of 50 mA was maintained throughout the reaction. The mixture was electrolysed for 120 minutes (4Q), filtered and the solvent removed *in vacuo*. The resulting solid was washed with water, filtered and recrystallised from $CHCl_3/Et_2O$, producing **1c** as a white solid. Yield: 0.16 g, 0.43 mmol (44 %).

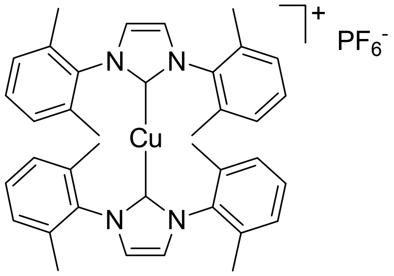
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H, ArH), 7.20 (d, *J* = 7.3 Hz, 4H, ArH), 7.10 (s, 2H, CH), 2.16 (s, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 179.0, 137.6, 135.1, 129.8, 129.0, 122.3, 18.0.

HRMS (ESI^+): Calcd for $C_{21}H_{24}CuN_2$ $[M–Cl+MeCN]^+$: 380.1183. Found: 380.1172.

Anal. Calcd for $C_{19}H_{20}ClCuN_2.½H_2O$: C, 59.37; H, 5.51; N, 7.29. Found: C, 59.55; H, 5.30; N, 7.15.

Bis[1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene]copper(I) hexafluorophosphate (1d)



1b (0.42 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 40 mA for 200 minutes (5Q), filtered and the solvent removed *in vacuo* producing a pale green solid. The solid was dissolved in acetone and filtered through celite to remove the insoluble green particulates. The solvent was removed from the filtrate *in vacuo* producing **1d** as an off-white solid. Yield: 0.14 g, 0.18 mmol (36 %). Single crystals suitable for X-ray analysis were grown by vapour diffusion of Et_2O in to a concentrated acetone solution of the product.

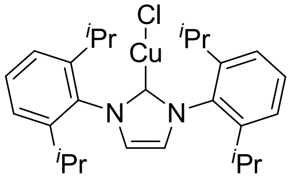
^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 7.52 (s, 2H, CH), 7.42 (t, *J* = 7.5 Hz, 2H, ArH), 7.26 (d, *J* = 7.5 Hz, 4H, ArH), 1.78 (s, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$) δ 178.1, 138.3, 135.9, 130.7, 129.6, 124.0, 17.5.

HRMS (ESI^+): Calcd for $C_{38}H_{40}CuN_4$ $[M–PF_6]^+$: 615.2543. Found: 615.2558.

Anal. Calcd for $C_{38}H_{40}CuF_6N_4P.½H_2O$: C, 59.25; H, 5.37; N, 7.27. Found: C, 59.15; H, 5.25; N, 7.35.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I)chloride (2c)



2a (0.42 g, 1 mmol) was added to a three-necked round-bottomed. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 60 mA for 80 minutes (3Q), filtered and the solvent removed *in vacuo*. The resulting solid was washed with Et_2O to yield **2c** as an off-white solid. Yield: 0.30 g, 0.62 mmol (62 %).

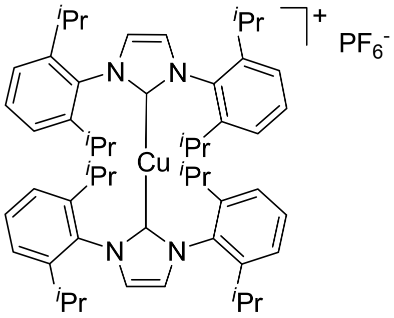
^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.70 (s, 2H, CH), 7.55 (t, J = 7.7 Hz, 2H, ArH), 7.41 (d, J = 7.7 Hz, 4H, ArH), 2.67 (m, 4H, $CH(CH_3)_2$), 1.31 (d, J = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.25 (d, J = 6.9 Hz, 12H, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$) δ 180.9, 146.6, 135.8, 131.2, 124.9, 29.5, 25.0, 24.0.

HRMS (ESI$^+$): Calcd for $C_{27}H_{36}ClCuN_2Na$ $[M+Na]^+$: 509.1775. Found: 509.1734.

Anal. Calcd for $C_{27}H_{36}ClCuN_2$: C, 66.51; H, 7.44; N, 5.75. Found: C, 66.30; H, 7.45; N, 5.70.

Bis[1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) hexafluorophosphate (2d)



2b (0.53 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 50 mA for 300 minutes (10Q), filtered and the solvent removed *in vacuo* producing an off-white solid. Repeated recrystallisation from acetone/pentane yielded **2d** as a white crystalline solid. Yield: 0.21 g, 0.21 mmol (42 %).

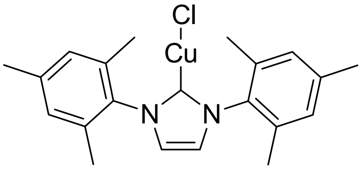
^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.55 (s, 4H, CH), 7.54 (t, *J* = 7.8 Hz, 4H, ArH), 7.25 (d, *J* = 7.8 Hz, 8H, ArH), 2.41 (hept, *J* = 6.9 Hz, 8H, C*H*$(CH_3)_2$), 1.04 (d, *J* = 6.9 Hz, 24H, CH$(CH_3)_2$), 0.94 (d, *J* = 6.9 Hz, 24H, CH$(CH_3)_2$).

^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 178.3, 146.0, 135.9, 131.5, 126.7, 125.4, 29.5, 24.8, 24.5.

HRMS (ESI$^+$): Calcd for $C_{54}H_{72}CuN_4$ $[M\text{-}PF_6]^+$: 839.5048. Found: 839.5071.

Anal. Calcd for $C_{54}H_{72}CuF_6N_4P$: C, 65.80; H, 7.36; N, 5.68. Found: C, 65.55; H, 7.35; N, 5.55.

[1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene]copper(I)chloride (3c)



2a (0.34 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The potential across the electrodes was adjusted so that a current of 50 mA was maintained throughout the reaction. The mixture was electrolysed at 50 mA for 19 minutes (Q), filtered and the solvent removed *in vacuo*. The solid was washed with petroleum ether and THF and dried *in vacuo* producing **3c** as a white crystalline solid. Yield: 0.24 g, 0.59 mmol (59 %).

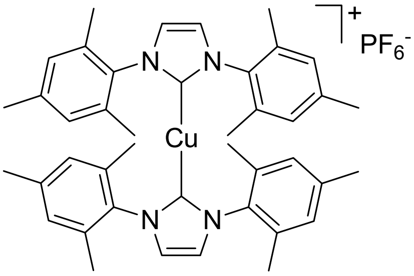
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H, CH), 6.99 (br, 4H, ArH), 2.34 (s, 6H, CH_3), 2.10 (s, 12H, CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 179.3, 139.8, 135.5, 135.0, 129.9, 122.8, 21.5, 18.2.

HRMS (ESI$^+$): Calcd for $C_{24}H_{28}CuN_2$ $[M\text{–}Cl\text{+}MeCN]^+$: 408.1496. Found: 408.1496.

Anal. Calcd for $C_{21}H_{24}CuClN_2$: C, 62.52; H, 6.00; N, 6.94. Found: C, 62.30; H, 5.95; N, 6.75.

Bis[1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene]copper(I) hexafluorophosphate (3d)



3b (0.45 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 100 mA for 220 minutes (14Q). The mixture was filtered through celite and the solvent reduced to 5 mL *in vacuo*. Water (50 mL) was added resulting in a white precipitate which was collected by filtration. The crude product was recrystallised from $CHCl_3/Et_2O$ producing **3d** as a white crystalline solid. Yield: 0.30 g, 0.37 mmol (74 %).

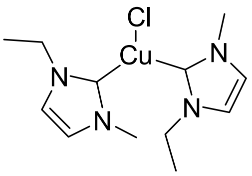
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 4H, CH), 6.89 (s, 8H, ArH), 2.42 (s, 12H, CH_3), 1.67 (s, 24H, CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 177.6, 139.6, 134.7, 134.6, 129.3, 122.9, 21.3, 17.1.

HRMS (ESI$^+$): Calcd for $C_{42}H_{48}CuN_4$ [M-PF$_6$]$^+$: 671.3170. Found: 671.3180.

Anal. Calcd for $C_{42}H_{48}CuF_6N_4P$: C, 61.72; H, 5.92; N, 6.85. Found: C, 61.55; H, 5.95; N, 6.70.

Bis(1-methyl-3-ethylimidazolin-2-ylidene)copper(I)bromide (4c)



4a (0.15 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 60 mA for 60 minutes (2Q). The solvent was removed *in vacuo* and the residue was washed with Et_2O to yield **4c** as an off-white solid. Due to the oily and sticky nature of **4c** an accurate yield could not be obtained.

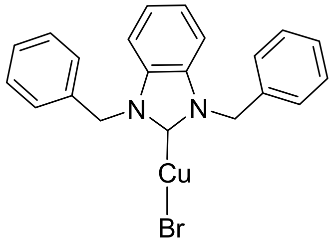
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H, CH), 6.90 (s, 2H, CH), 4.13 (q, J = 6.6 Hz, 4H, CH_2), 3.79 (s, 6H, NCH_3), 1.42 (t, J = 6.6 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 176.0, 121.9, 120.2, 46.4, 38.3, 17.1.

HRMS (ESI$^+$): Calcd for $C_{12}H_{20}CuN_4$ [M-Cl]$^+$: 283.0978. Found: 283.0991.

Due to the extremely air-sensitive nature of **4c**, elemental analysis was not performed.

(1,3-Dibenzylbenzimidazolin-2-ylidene)copper(I)bromide (5c)



5a (0.38 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added forming a suspension. The copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture and the mixture was electrolysed at 50 mA for 45 minutes (1.5Q). The mixture was filtered and the solvent was removed *in vacuo*. The resulting solid was washed with MeOH, dissolved in CH_2Cl_2 and filtered, and the solvent removed *in vacuo*, to produce **5c** as an off-white solid. This was recrystallised from CH_2Cl_2/Et_2O. Yield: 0.30 g, 0.68 mmol (68 %). Single crystals suitable for X-ray analysis were grown by vapour diffusion of pentane in to a concentrated CH_2Cl_2 solution of the product.

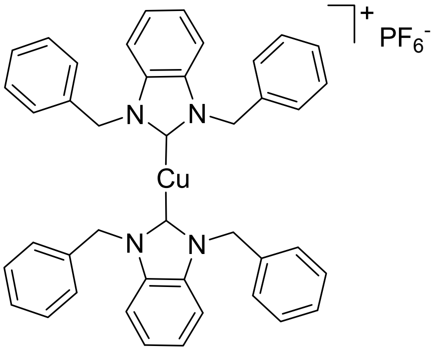
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 – 7.32 (m, 12H, ArH), 7.30 – 7.27 (m, 2H, ArH), 5.69 (s, 4H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ (Cu-C not observed), 135.9, 129.6, 129.0, 128.0, 124.7, 112.5, 53.4.

HRMS (ESI$^+$): Calcd for $C_{21}H_{18}CuN_2$ [M–Br]$^+$: 361.0761. Found: 361.0771.

Anal. Calcd for $C_{21}H_{18}BrCuN_2$: C, 57.09; H, 4.11; N, 6.34. Found: C, 56.90; H, 4.05; N, 6.15.

(1,3-Dibenzylbenzimidazolin-2-ylidene)copper(I) hexafluorophosphate (5d)



5b (0.44 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 50 mA for 330 minutes (11Q). The mixture was filtered and the solvent removed *in vacuo* to yield a brown solid. This was washed with THF (5 mL) and dissolved in CH_2Cl_2 and filtered. The solvent was removed *in vacuo* to give **5d** as a white crystalline solid. Yield: 0.26 g, 0.32 mmol (64 %). Single crystals suitable for X-ray diffraction analysis were grown by the vapour diffusion of pentane in to a concentrated CH_2Cl_2 solution of the product.

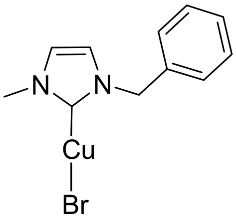
^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 7.68 (dd, *J* = 6.1, 3.1 Hz, 4H, CH), 7.42 (dd, *J* = 6.1, 3.1 Hz, 4H, CH), 7.39 – 7.23 (m, 20H, ArH), 5.71 (s, 8H, CH_2).

$^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$) δ 176.5, 137.1, 134.9, 130.0, 129.2, 128.5, 125.3, 113.1, 52.9.

HRMS (ESI$^+$): Calcd for $C_{42}H_{36}CuN_4$ $[M-PF_6]^+$: 659.2230. Found: 659.2227.

Anal. Calcd for $C_{42}H_{36}CuF_6N_4P.H_2O$: C, 61.27; H, 4.65; N, 6.81. Found: C, 61.55; H, 4.55; N, 6.80.

(1-Methyl-3-benzylimidazolin-2-ylidene)copper(I)bromide (6c)



6a (0.25 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added forming a suspension. The copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture and the mixture was electrolysed at 50 mA for 60 minutes (2Q). The mixture was filtered and the solvent was removed *in vacuo*. The product was extracted into THF from the resulting yellow oil, and the solvent removed *in vacuo* to give **6c** as colourless crystals. Yield: 0.21 g, 0.67 mmol (67 %). Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated THF solution of the product.

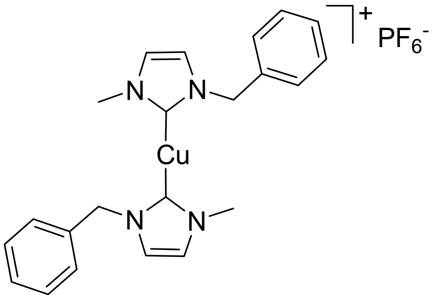
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 5H, ArH), 6.87 (d, *J* = 1.7 Hz, 1H, CH), 6.82 (d, *J* = 1.7 Hz, 1H, CH), 5.22 (s, 2H, CH_2), 3.73 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 178.7, 135.8, 129.6, 129.2, 128.1, 122.2, 120.7, 55.3, 38.4.

HRMS (ESI$^+$): Calcd for $C_{15}H_{19}CuN_4$ [M–Br+2MeCN]$^+$: 317.0822. Found: 317.0834.

Anal. Calcd for $C_{11}H_{12}BrCuN_2$: C, 41.85; H, 3.83; N, 8.87. Found: C, 41.55; H, 3.95; N; 9.15.

Bis(1-methyl-3-benzylimidazolin-2-ylidene)copper(I)hexafluorophosphate (6d)



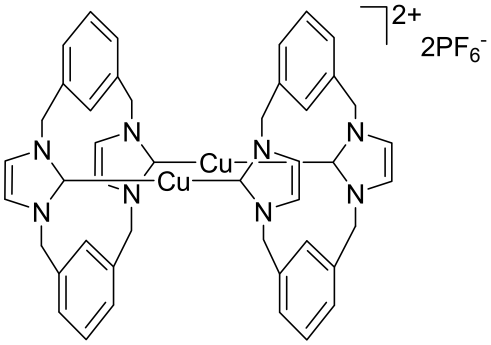
6b (0.32 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 50 mA for 150 minutes (5Q). CH_2Cl_2 was added to the solid and the suspension was filtered. The CH_2Cl_2 was allowed to evaporate, yielding colourless crystals of **6d**. Yield: 0.16 g, 0.29 mmol (58 %).

^{1}H NMR (75 MHz, CD_3CN) δ 7.40 – 7.22 (m, 10H, ArH), 7.11 (d, *J* = 1.8 Hz, 2H, CH), 7.09 (d, *J* = 1.8 Hz, 2H, CH), 5.25 (s, 4H, CH_2), 3.74 (s, 6H, CH_3).

$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN) δ 179.1, 138.3, 129.8, 129.0, 128.6, 123.3, 122.2, 54.9, 38.5.

HRMS (ESI$^+$): Calcd for $C_{22}H_{24}CuN_4$ $[M–PF_6]^+$: 407.1291. Found: 407.1291.

Macrocyclic Copper Complex (7d)



7b (0.63 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 10 mA for 880 minutes (5.5Q). The mixture was filtered through celite and the solvent was removed *in vacuo*. Recrystallisation from MeCN/H_2O followed by washing with MeOH and Et_2O gave **7d** as a white crystalline solid. Yield: 0.39 g, 0.36 mmol (72 %). Single crystals suitable for X-ray analysis were grown by vapour diffusion of Et_2O in to a concentrated MeCN solution of the product.

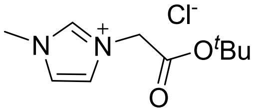
^1H NMR (500 MHz, DMSO-d_6) δ 7.26 (t, J = 7.6 Hz, 4H, ArH), 7.20 (s, 8H, CH), 7.15 (d, J = 7.6 Hz, 8H, ArH), 5.69 (s, 4H, ArH), 5.16 (s, 16H, CH_2).

$^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6) δ 177.5, 138.0, 128.5, 126.0, 122.7, 119.8, 52.7.

HRMS (ESI$^+$): Calcd for $C_{22}H_{20}CuN_4$ $[M–2PF_6]^{2+}$: 403.0978. Found: 403.0997.

Anal. Calcd for $C_{44}H_{40}Cu_2F_{12}N_8P_2$: C, 48.14; H, 3.67; N, 10.21. Found: C, 48.15; H, 3.60; N; 10.20.

1-Methyl-2-*tert*-butylacetate imidazolium chloride (8a)



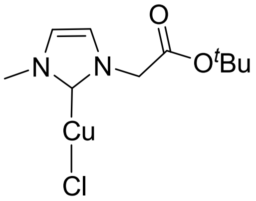
1-Methylimidazole (1.6 mL, 20 mmol) and *tert*-butyl 2-chloroacetate (2.9 mL, 20 mmol) were stirred at room temperature for 18 hours during which time the mixture solidified. Recrystallisation from CH_2Cl_2/hexane followed by washing with Et_2O and drying in *vacuo* gave **8a** as a white hygroscopic solid. Yield: 3.59 g, 15.4 mmol (77 %).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.31 (s, 1H, CH), 7.78 (s, 2H, CH), 5.22 (s, 2H, CH_2), 3.91 (s, 3H, CH_3), 1.44 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ 165.8, 137.7, 123.6, 123.1, 82.9, 49.5, 35.7, 27.6.

HRMS (ESI$^+$): Calcd for $C_{10}H_{17}N_2O_2$ $[M–Cl]^+$: 197.1285. Found: 197.1307.

(1-Methyl-3-*tert*-butylacetateimidazolin-2-ylidene)copper(I)chloride (8c)



8a (0.23 g, 1 mmol) was added to a three-necked round-bottomed flask. Anhydrous MeCN (15 mL) was added and the copper electrodes (1 x 3 cm^2) were inserted in to the reaction mixture. The mixture was electrolysed at 60 mA for 50 minutes (2Q). The mixture was filtered and the solvent was removed *in vacuo* to yield **8c** as an off-white solid. Yield: 0.14 g, 0.48 mmol (48 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1H, CH), 6.93 (s, 1H, CH), 4.78 (s, 2H, CH_2), 3.81 (s, 3H, CH_3), 1.45 (s, 9H, CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 178.0, 166.4, 122.0, 83.7, 52.6, 38.2, 28.0.

HRMS (ESI$^+$): Calcd for $C_{12}H_{19}CuN_3O_2$ $[M–Cl+MeCN]^+$: 300.0768. Found: 300.0761.

Anal. Calcd for $C_{10}H_{16}ClCuN_2O_2$. 1/3CH_2Cl_2: C, 38.36; H, 5.19; N, 8.66. Found: C, 38.40; H, 5.15; N; 8.70.

2. Crystallographic details

Crystals were mounted under oil on glass fiber and X-ray diffraction data for **1d, 5d, 6c** and **7d** were collected at 150(1)K with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) using Bruker Nonius X-8 diffractometer with ApexII detector and FR591 rotating anode generator. Data sets were corrected for absorption using a multiscan method, and structures were solved by direct methods using SHELXS-97[5] and refined by full-matrix least-squares on F2 by SHELXL-97,[5] interfaced through the program X-Seed.[6]

Diffraction data for **5c** were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "Crysalis".[7] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[8] OLEX2[9] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithm used for structure solution was direct methods using the SHELXS-97.[10] Refinement by full-matrix least-squares used the SHELXL-97[11] algorithm within OLEX2.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Crystallographic details for 1d

Empirical formula	$C_{38}H_{40}CuF_6N_4P$	
Formula weight	761.25	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.0778(4) Å	α = 90°
	b = 15.5817(5) Å	β = 102.4220(10)°
	c = 17.3053(4) Å	γ = 90°
Volume	3707.16(18) $Å^3$	
Z	4	
Density (calculated)	1.364 g/cm^3	
Absorption coefficient	0.695 mm^{-1}	
F(000)	1576	
Crystal size	0.65 x 0.32 x 0.21 mm^3	
Theta range for data collection	1.78 to 28.31°	
Index ranges	-18<=h<=18, -20<=k<=20, -20<=l<=23	
Reflections collected	58537	
Independent reflections	9198 [R(int) = 0.0789]	
Completeness to theta = 28.31°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8678 and 0.6609	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9198 / 0 / 459	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1001	
R indices (all data)	R1 = 0.0536, wR2 = 0.1102	
Largest diff. peak and hole	0.508 and -0.543 e.$Å^{-3}$	

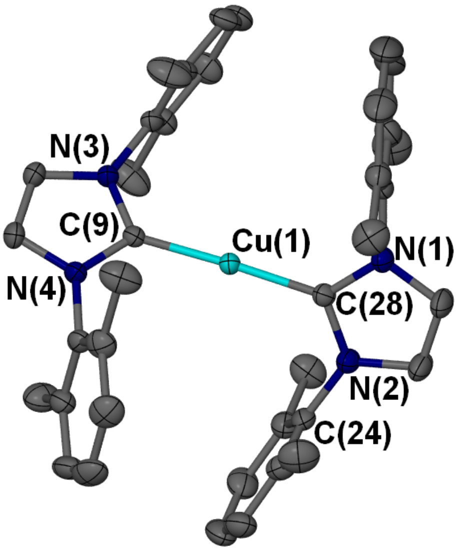


Figure S1 Solid-state structure of **1d**. Selected bond distances (Å) and lengths (deg): C(9)-Cu(1) 1.8918(17), C(28)-Cu(1) 1.8873(17), C(28)-N(2) 1.354(2), N(2)-C(24) 1.441(2), C(9)-Cu(1)-C(28) 177.55(7), Cu(1)-C(28)-N(1) 130.74(13), N(1)-C(28)-N(2) 104.03(14), C(28)-N(2)-C24 124.03(15).

Crystallographic details for 5c

Empirical formula	$C_{42} H_{36} Br_2 Cu_2 N_4$	
Formula weight	883.65	
Temperature	110.00(10) K	
Wavelength	0.7107 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.4581(6) Å	α= 69.206(7)°.
	b = 9.5482(7) Å	β= 82.837(6)°.
	c = 11.2949(10) Å	γ = 69.262(6)°.
Volume	891.80(12) $Å^3$	
Z	1	
Density (calculated)	1.645 g/cm^3	
Absorption coefficient	3.470 mm^{-1}	
F(000)	444	
Crystal size	0.217 x 0.1108 x 0.0626 mm^3	
Theta range for data collection	3.00 to 31.32°.	
Index ranges	-11<=h<=13, -13<=k<=13, -15<=l<=15	
Reflections collected	8485	
Independent reflections	5176 [R(int) = 0.0285]	
Completeness to theta = 29.07°	99.56 %	
Absorption correction	Analytical	
Max. and min. transmission	0.827 and 0.579	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5176 / 0 / 226	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0877	
R indices (all data)	R1 = 0.0539, wR2 = 0.0953	
Largest diff. peak and hole	1.177 and -0.757 e.$Å^{-3}$	

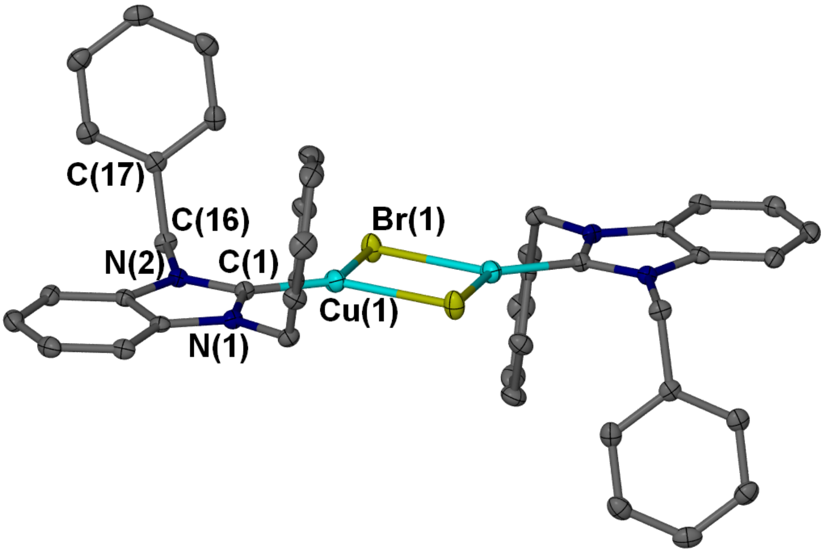


Figure S2 Solid-state structure of **5c**. Selected bond distances (Å) and lengths (deg): C(1)-Cu(1) 1.914(3), Cu(1)-Br(1) 2.5073(5), C(1)-N(1) 1.369(3), C(1)-Cu(1)-Br(1) 125.58(8), N(2)-C(1)-Cu(1) 128.60(19), C(17)-C(16)-N(2) 111.9(2).

Crystallographic details for 5d

Empirical formula	C42 H36 Cu F6 N4 P	
Formula weight	805.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0929(10) Å	α= 69.473(5)°.
	b = 10.7824(15) Å	β= 86.792(4)°.
	c = 11.7655(16) Å	γ = 69.242(4)°.
Volume	896.3(2) $Å^3$	
Z	1	
Density (calculated)	1.492 g/cm^3	
Absorption coefficient	0.723 mm^{-1}	
F(000)	414	
Crystal size	0.18 x 0.11 x 0.08 mm^3	
Theta range for data collection	1.85 to 26.51°.	
Index ranges	-7<=h<=10, -13<=k<=13, -14<=l<=14	
Reflections collected	12286	
Independent reflections	3698 [R(int) = 0.0258]	
Completeness to theta = 26.51°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9444 and 0.8808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3698 / 0 / 247	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0746	
R indices (all data)	R1 = 0.0310, wR2 = 0.0770	
Largest diff. peak and hole	0.302 and -0.246 e.$Å^{-3}$	

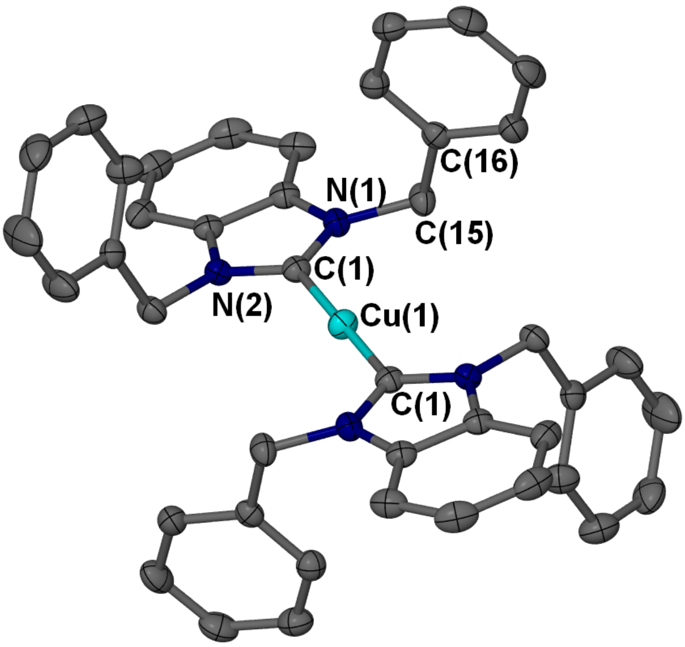


Figure S3 Solid-state structure of **5d**. Selected bond distances (Å) and lengths (deg): C(1)-Cu(1) 1.9066(15), C(1)-N(1) 1.3523(19), C(1)-Cu(1)-C(1) 180.00(7), N(1)-C(1)-Cu(1) 126.41(11), C(16)-C(15)-C(1) 112.98(12).

Crystallographic details for 6c

Identification code	e:r~1~1	
Empirical formula	C22 H24 Br2 Cu2 N4	
Formula weight	631.35	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.8647(9) Å	α= 90°.
	b = 7.3597(7) Å	β= 95.924(4)°.
	c = 16.2732(16) Å	γ = 90°.
Volume	1175.15(19) Å^3	
Z	2	
Density (calculated)	1.784 g/cm^3	
Absorption coefficient	5.226 mm^{-1}	
F(000)	624.33	
Crystal size	0.56 x 0.14 x 0.05 mm^3	
Theta range for data collection	2.31 to 30.34°.	
Index ranges	-14<=h<=14, -9<=k<=10, -23<=l<=23	
Reflections collected	20429	
Independent reflections	3513 [R(int) = 0.0395]	
Completeness to theta = 30.34°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.876 and 0.648	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3513 / 0 / 137	
Goodness-of-fit on F^2	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.2323	
R indices (all data)	R1 = 0.0783, wR2 = 0.2401	
Largest diff. peak and hole	1.612 and -2.697 e.Å^{-3}	

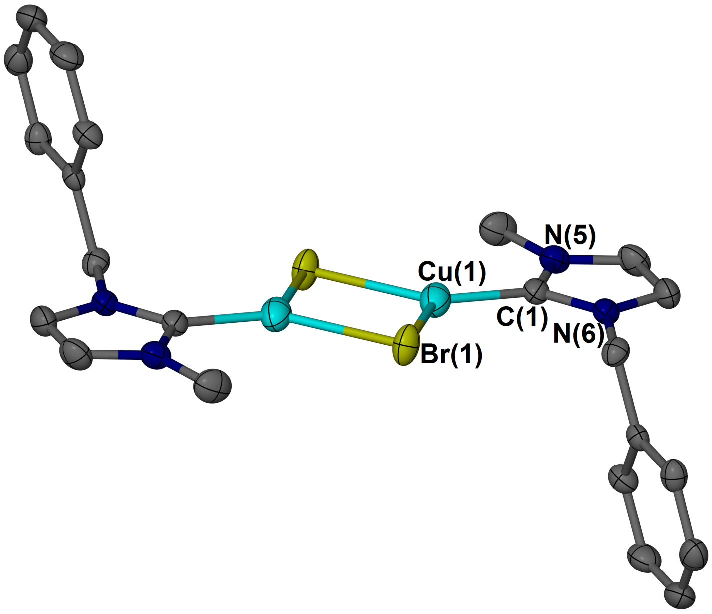


Figure S4 Solid-state structure of **6c**. Selected bond distances (Å) and lengths (deg): C(1)-Cu(1) 1.932(6), Cu(1)-Br(1) 2.4506(13), C(1)-N(6) 1.363(7), C(1)-Cu(1)-Br(1) 127.94(18), Cu(1)-C(1)-N(6) 126.2(4), N(6)-C(5)-C(6) 112.8(4).

Crystallographic details for 7d

Empirical formula	$C_{44}H_{40}Cu_2F_{12}N_8P_2$	
Formula weight	1097.88	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.7429(13) Å	α= 90°.
	b = 11.0137(17) Å	β= 92.910(4)°.
	c = 23.226(4) Å	γ = 90°.
Volume	2233.6(6) $Å^3$	
Z	2	
Density (calculated)	1.632 g/cm^3	
Absorption coefficient	1.118 mm^{-1}	
F(000)	1112	
Crystal size	0.39 x 0.30 x 0.14 mm^3	
Theta range for data collection	2.05 to 28.38°.	
Index ranges	-11<=h<=11, -14<=k<=14, -30<=l<=29	
Reflections collected	38495	
Independent reflections	5563 [R(int) = 0.0332]	
Completeness to theta = 28.38°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8592 and 0.6696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5563 / 0 / 307	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0775	
R indices (all data)	R1 = 0.0345, wR2 = 0.0799	
Largest diff. peak and hole	0.360 and -0.302 $e.Å^{-3}$	

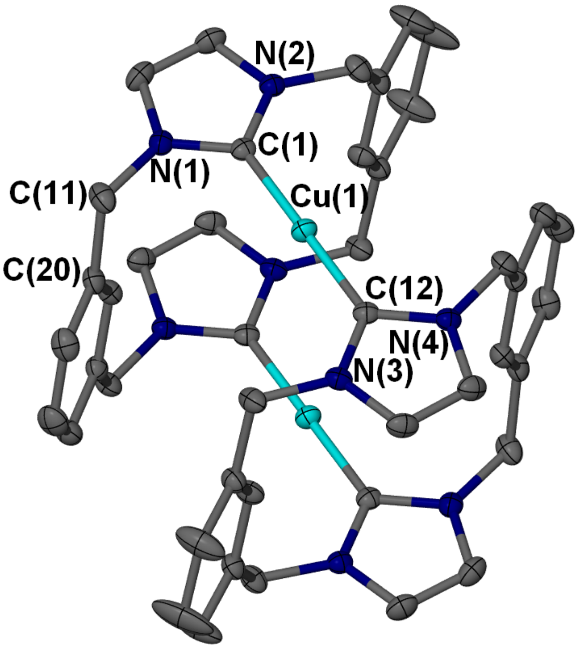


Figure S5 Solid-state structure of **7d**. Selected bond distances (Å) and lengths (deg): C(1)-Cu(1) 1.8966(17), C(12)-Cu(1) 1.8952(17), C(1)-N(1) 1.355(2), C(1)-Cu(1)-C(12) 178.45(7), Cu(1)-C(1)-N(1) 128.41(13), C(1)-N(1)-C(11) 124.74(15), N(1)-C(11)-C(20) 115.13(15).

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