Supplementary Material (ESI) for Chemical Communications

Supporting Information

Facile Synthesis of Metal N-Heterocyclic Carbene Complexes

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□. General Information

All the chemicals were obtained from commercial suppliers and used without further purification. The imidazoium salts were prepared according to known procedures.[1-5] The Ag-NHC complexes were prepared from imidazoium salts and Ag_2O in acetonitrile. The metal plates are commercially available and burnished before used. Elemental analyses were performed on a Flash EA1112 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from TMS at $\delta = 0$ ppm, and coupling constants (J) are expressed in Hz.

□. Experimental Details

Method A:

All of the experiments were carried out at the room temperature (about 25 °C). The reactions were carried out in a galss cell (20 mL). Metal plate (1 x 2 cm^2) was used as the anode, and platinum foil (1 x 1 cm^2) was used as the cathode. A solution of imidazoium salts (1.0 mmol) in 10 mL of acetonitrile was electrolyzed. Potential across the electrodes was adjusted so that a current of 50 mA passed through the solution under galvanostatic control. The reaction mixture was stirred with the help of a magnetic stirrer during the progress of the reaction. The evolving hydrogen was removed with a stream of N_2. After passing through 1.0 F/mol of electricity, the solution was filtered through silica gel to remove a small amount of insoluble solid. The filtrate was then evaporated to dryness, washed with diethyl ether and dried. Recrystallization of the crude product by slow diffusion of diethyl ether to its acetonitrile solution gave fine crystals.

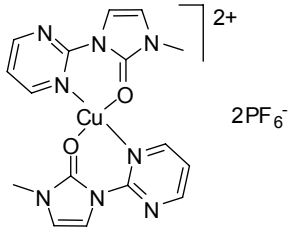
Method B:

The silver N-heterocyclic carbene complexes were used instead of imidazoium salts as the NHC sources. Imidazoium salts (1.0 mmol) was added to a slurry of Ag_2O (0.5 mmol) in 10 mL of CH_3CN. The mixture was protected from light and stirred at 50 ºC for few

hours. The solution was filtered through silica to remove a small amount of unreacted Ag_2O. The clear filtrate was then used as the electrolyte and electrolyzed at room temperature. Potential across the electrodes was adjusted so that a current of 50 mA passed through the solution under galvanostatic control. The reaction mixture was stirred with the help of magnetic stirrer during the progress of the reaction. After passing through 1.0 F/mol of electricity, the solution was filtered through silica gel to remove a small amount of insoluble solid. The filtrate was then evaporated to dryness, washed with diethyl ether and dried. Recrystallization of the crude product by slow diffusion of diethyl ether to its acetonitrile solution gave fine crystals.

Synthesis of [Cu^{II}(1-methyl-3-(pyrimidin-2-yl)-1H-imidazol-2(3H)-one)$_2$]$(PF_6)_2$, 1. A solution of 1-methyl-3-(pyrimidin-2-yl)imidazolium hexafluorophosphate (306 mg, 1.0 mmol) in 10 mL of CH_3CN was treated with copper powder (38 mg, 0.6 mmol). The mixture was allowed to react at 80 ºC for 2 days in air. The solution was filtered through silica to remove unreacted copper. The filtrate was concentrated to *ca* 2 mL. The compound was obtained by adding diethyl ether to the filtrate.

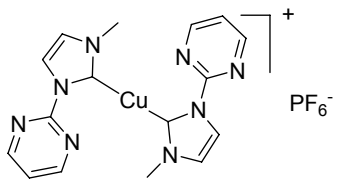
. Analytical and Spectroscopic Data of Compounds 1-14



[Cu(1-methyl-3-(pyrimidin-2-yl)-1H-imidazol-2(3H)-one)$_2$]$(PF_6)_2$, 1

Yield: 192 mg (54.4%).

Green solid. Calcd for $C_{16}H_{16}F_{12}N_8O_2P_2Cu$: C, 27.23; H, 2.28; N, 15.88. Found: C, 27.19; H, 2.23; N, 15.96.



[Cu(1-methyl-3-pyrimidinylimidazolylidene)$_2$]PF_6, 2

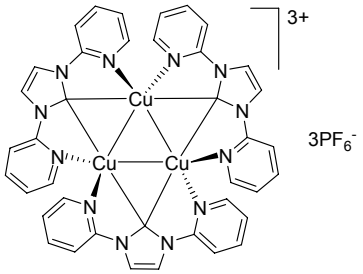
Method A

Yield: 236 mg (89.2%). Calcd for $C_{16}H_{16}F_6N_8PCu$: C, 36.34; H, 3.05; N, 21.19. Found: C, 36.51; H, 2.99; N, 20.91.

Method B

Yield: 245 mg (92.6%). Calcd for $C_{16}H_{16}F_6N_8PCu$: C, 36.34; H, 3.05; N, 21.19. Found: C, 36.41; H, 3.00; N, 20.85.

Yellow solid. ^{1}H NMR (CD_3CN): 8.78 (s, *o*-$C_4H_3N_2$, 4H), 8.18 (s, NCHCHN, 2H), 7.67 (s, NCHCHN, 2H), 7.51 (br, *m*- $C_4H_3N_2$, 2H), 3.85 (s, CH_3, 6H). ^{13}C NMR (CD_3CN): 183.6 (Cu-C), 159.6, 155.9, 125.1, 120.9, 117.7, 38.9.



[Cu_3(1,3-dipyridylimidazolylidene)$_3$](PF_6)$_3$, 3

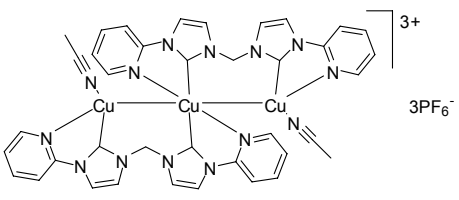
Method A

Yield: 338 mg (78.5%). Anal. Calcd for $C_{39}H_{30}F_{18}N_{12}P_3Cu_3$: C, 36.25; H, 2.34; N, 13.01. Found: C, 35.97; H, 2.34; N, 12.87.

Method B

Yield: 367 mg (85.2%). Anal. Calcd for $C_{39}H_{30}F_{18}N_{12}P_3Cu_3$: C, 36.25; H, 2.34; N, 13.01. Found: C, 35.89; H, 2.32; N, 12.93.

Yellow solid. ^{1}H NMR (dmso-d_6): 8.83, (br, *o*-C_5H_4N, 6H), 8.37 (br, *m*-C_5H_4N, 6H), 8.29(br, NCHCHN, 6H), 7.51 (br, *p*-C_5H_4N, 6H), 7.45 (m, *m*-C_5H_4N, 6H). ^{13}C NMR (dmso-d_6): 170.7 (Cu-C), 149.3, 147.1, 142.5, 125.8, 124.6, 116.1.



[Cu_3(bis(pyridylimidazolylidenyl)methane)$_2$(CH_3CN)$_2$](PF_6)$_3$, 4 [6]

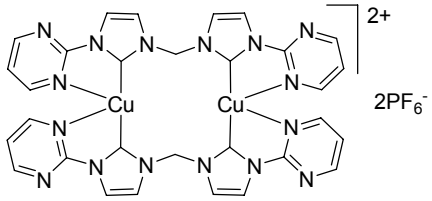
Method A

Yield: 512 mg (83.3%). Anal. Calcd for $C_{34}H_{28}F_{18}N_{12}P_3Cu_3$: C, 33.19; H, 2.29; N, 13.66. Found: C, 33.24; H, 2.31; N, 13.64.

Method B

Yield: 580 mg (94.3%). Anal. Calcd for $C_{34}H_{28}F_{18}N_{12}P_3Cu_3$: C, 33.19; H, 2.29; N, 13.66. Found: C, 33.37; H, 2.35; N, 13.86.

Red solid. ^{1}H NMR (dmso-d_6): 8.22 (s, *o*-C_5H_4N, 4H), 7.87 - 7.83 (m, *p*-C_5H_4N + NCHCHN, 8H), 7.74 (br, *m*-C_5H_4N + NCHCHN, 8H), 7.23 (t, J = 6.0 Hz, *m*- C_5H_4N, 4H), 6.49 (s, NCH_2N, 4H).



[Cu_2(bis(pyrimidylimidazolylidenyl)methane)$_2$](PF_6)$_2$, 5 [6]

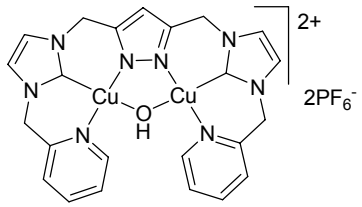
Method A

Yield: 396 mg (77.2%). Calcd for $C_{30}H_{24}F_{12}N_{16}P_2Cu_2$: C, 35.13; H, 2.36; N, 21.85. Found: C, 35.30; H, 2.54; N, 21.80.

Method B

Yield: 462 mg (90.1%). Calcd for $C_{30}H_{24}F_{12}N_{16}P_2Cu_2$: C, 35.13; H, 2.36; N, 21.85. Found: C, 35.27; H, 2.39; N, 21.94.

Red solid. ^{1}H NMR (dmso-d_6): 8.52 (d, J = 3.6 Hz, *o*-$C_4H_3N_2$, 8H), 8.04, 7.79 (both s, NCHCHN, each 4H), 7.41 (t, J = 4.8 Hz, *m*-$C_4H_3N_2$, 4H), 6.48 (s, NCH_2N, 4H).

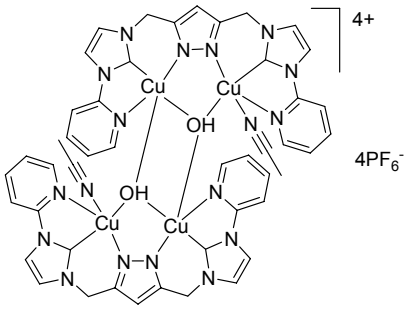


[Cu_2(3,5-bis(N-picolylimidazolylidenylmethyl)pyrazolate)(OH)](PF_6)$_2$, 6 [8]

Method A

Yield: 580 mg, (68.8%).

Red solid. Anal. Calcd for $C_{23}H_{22}F_{12}N_8OP_2Cu_2$: C, 32.75; H, 2.63; N, 13.28. Found: C, 32.91; H, 2.60; N, 12.97.

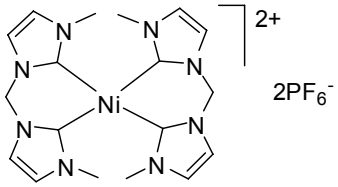


[Cu_4(3,5-bis(N-pyridylimidazolylidenylmethyl)pyrazolate)$_2$$(OH)_2(CH_3CN)_2](PF_6)_4$, 7 [8]

Method A

Yield: 515 mg, (60.1%).

Red-brown solid. Anal. Calcd for $C_{46}H_{42}F_{24}N_{18}O_2P_4Cu_4$: C, 32.25; H, 2.47; N, 14.72. Found: C, 32.22; H, 2.42; N, 14.43.

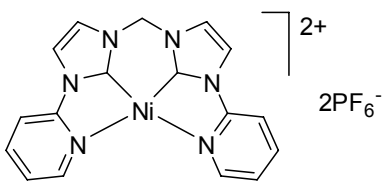


[Ni(bis(1-methylimidazolylidenyl)methane$_2$](PF$_6$)$_2$, 8 [7]

Method A

Yield: 151 mg (43.1%).

Pale-yellow solid. Calcd for $C_{18}H_{24}F_{12}N_8P_2Ni$: C, 30.84; H, 3.45; N, 15.98. Found: C, 31.08; H, 3.43; N, 15.86. ^{1}H NMR (dmso-d_6): 7.73 (d, J = 1.6 Hz, NCHCHN, 4H), 7.34 (d, J = 1.6 Hz, NCHCHN, 4H), 6.95, 6.45 (both d, J = 12.8 Hz, NCH_2N, each 2H), 3.20 (s, CH_3, 12H).



[Ni(bis(N-pyridylimidazolylidenyl)metahne)](PF$_6$)$_2$, 9 [3]

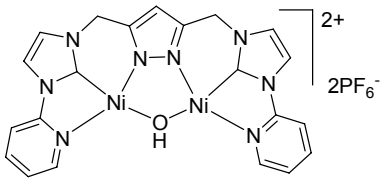
Method A

Yield: 356 mg (54.7%). Calcd for $C_{17}H_{14}F_{12}N_6P_2Ni$: C, 31.37; H, 2.17; N, 12.91. Found: C, 31.53; H, 2.12; N, 12.74.

Method B

Yield: 463 mg (71.1%). Calcd for $C_{17}H_{14}F_{12}N_6P_2Ni$: C, 31.37; H, 2.17; N, 12.91. Found: C, 31.50; H, 2.16; N, 12.83.

Brown-yellow solid. ^{1}H NMR (dmso-d_6): 8.88 (d, J = 5.6 Hz, *o*-C_5H_4N, 2H), 8.62 (d, J = 2.4 Hz, NCHCHN, 2H), 8.52 (t, J = 8.0 Hz, *p*-C_5H_4N, 2H), 8.30 (d, J = 8.0 Hz, *m*-C_5H_4N, 2H), 8.13 (d, J = 2.4 Hz, NCHCHN, 2H), 7.77 (t, J = 6.8 Hz, *m*-C_5H_4N, 2H), 6.68 (s, NCH_2N, 2H).

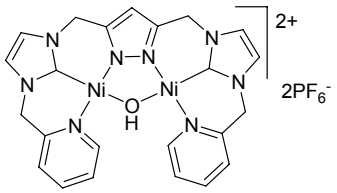


[Ni_2(3,5-bis(N-pyridylimidazolylidenylmethyl)pyrazolate)(OH)](PF_6)$_2$, 10 [5]

Method A

Yield: 260 mg (32.3%).

Yellow solid. Anal. Calcd for $C_{21}H_{18}F_{12}N_8OP_2Ni_2$: C, 31.30; H, 2.25; N, 13.91. Found: C, 31.52; H, 2.37; N, 13.71. ^{1}H NMR (dmso-d_6): 8.36 (d, J = 1.6 Hz, NCHCHN, 2H), 8.35-8.29 (m, *m*-C_5H_4N + *o*-C_5H_4N, 4H), 7.98 (d, J = 8.0 Hz, *m*-C_5H_4N, 2H), 7.71 (s, NCHCHN, 2H), 7.55 (t, J = 6.4 Hz, *p*-C_5H_4N, 2H), 6.39 (s, C_3HN_2, 1H), 5.47 (s, CH_2, 4H), 1.69 (s, OH, 1H).

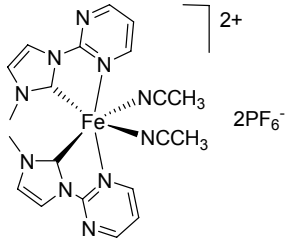


[Ni_2(3,5-bis(N-picolylimidazolylidenylmethyl)pyrazolate)(OH)](PF_6)$_2$, 11 [5]

Method A

Yield: 310 mg (37.2%).

Yellow solid. Anal. Calcd for $C_{23}H_{22}F_{12}N_8OP_2Ni_2$: C, 33.13; H, 2.66; N, 13.44. Found: C, 33.48; H, 2.84; N, 13.24. ^{1}H NMR (dmso-d_6): 9.03 (d, J = 6.0, o-C_5H_4N, 2H), 8.11 (t, J = 7.6 Hz, p-C_5H_4N, 2H), 7.72 (d, J = 7.6 Hz, m-C_5H_4N, 2H), 7.64 (s, NCHCHN, 2H), 7.60 (t, J = 7.6 Hz, m-C_5H_4N, 2H), 7.57 (s, NCHCHN, 2H), 6.39 (s, C_3HN_2,1H), 5.62 (s, CH_2, 4H), 5.37 (s, CH_2, 4H), 1.90 (s, OH, 1H).



[Fe(1-methyl-3-pyridylimidazolylidene)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$, 12

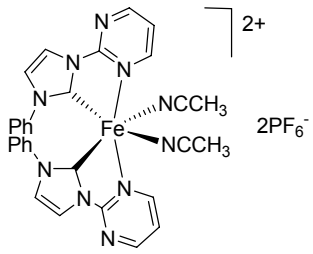
Method A

Yield: 126 mg (33.7%). Calcd for $C_{20}H_{22}F_{12}N_{10}P_2Fe$: C, 32.10; H, 2.96; N, 18.72. Found: C, 32.46; H, 2.98; N, 18.59.

Method B

Yield: 240 mg (64.2%). Calcd for $C_{20}H_{22}F_{12}N_{10}P_2Fe$: C, 32.10; H, 2.96; N, 18.72. Found: C, 32.51; H, 2.97; N, 18.86.

Red-brown solid. ^{1}H NMR (dmso-d_6): 9.18 (s, o-$C_4H_3N_2$, 2H), 9.03 (s, o-$C_4H_3N_2$, 2H), 8.40 (s, NCHCHN, 2H), 7.65 (s, m-$C_4H_3N_2$, 2H), 7.49 (s, NCHCHN, 2H), 2.72 (s, CH_3, 6H), 2.07 (s, CH_3CN, 6H). ^{13}C NMR (dmso-d_6): 201.0 (Fe-C), 164.1, 160.4, 158.7, 136.9, 129.5, 118.8, 118.4, 35.6, 1.5.



[Fe(1-phenyl-3-pyrimidylimidazolylidene)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$, 13

Method A

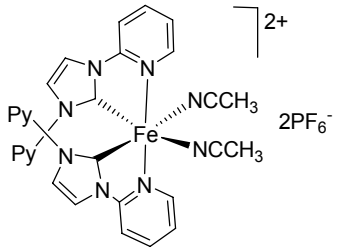
Yield: 98 mg (22.5%). Calcd for $C_{30}H_{26}F_{12}N_{10}P_2Fe$: C, 41.30; H, 3.00; N, 16.06. Found: C,

41.44; H, 3.05; N, 15.73.

Method B

Yield: 204 mg (46.8%). Calcd for $C_{30}H_{26}F_{12}N_{10}P_2Fe$: C, 41.30; H, 3.00; N, 16.06. Found: C, 41.39; H, 2.98; N, 15.82.

Red-brown solid. ^{1}H NMR (dmso-d_6): 8.67 (d, J = 4.4 Hz, o-$C_4H_3N_2$, 4H), 8.44 (s, NCHCHN, 2H), 7.76 (s, NCHCHN, 2H), 7.25 (t, J = 7.2 Hz, o-C_6H_5, 4H), 7.14 (t, J = 7.2 Hz, m-C_6H_5, 4H), 6.81 (s, m-$C_4H_3N_2$, 2H), 6.79 (s, p-C_6H_5, 2H). ^{13}C NMR (dmso-d_6): 202.8 (Fe-C), 163.6, 160.5, 158.3, 137.9, 129.9, 129.7, 129.5, 126.1, 119.0, 118.5 (CH_3CN), 118.2, 1.5(CH_3CN).



[Fe(1-phenyl-3-pyridylimidazolylidene)$_2$(CH_3CN)$_2$](PF_6)$_2$, 14

Method A

Yield: 105 mg (24.1%). Calcd for $C_{30}H_{26}F_{12}N_{10}P_2Fe$: C, 41.30; H, 3.00; N, 16.06. Found: C, 41.78; H, 3.12; N, 15.79.

Method B

Yield: 240 mg (55.0%). Calcd for $C_{30}H_{26}F_{12}N_{10}P_2Fe$: C, 41.30; H, 3.00; N, 16.06. Found: C, 41.67; H, 3.11; N, 15.87.

Red-brown solid. ^{1}H NMR (dmso-d_6): 8.31 (dd, J = 1.6, 5.2 Hz, o-C_5H_4NFe, 2H), 8.29 (d, J = 2.4 Hz, NCHCHN, 2H), 8.23 (dt, J = 1.6, 8.0 Hz, m-C_5H_4NFe, 2H), 8.17 (d, J = 8.0 Hz, m-C_5H_4NFe, 2H), 7.85 (dt, J = 2.0, 7.6 Hz, p-C_5H_4NFe, 2H), 7.38 (dd, J = 2.4, 7.2 Hz, o-C_5H_4N, 2H), 7.35 (d, J = 2.4 Hz, NCHCHN, 2H), 7.31 (dt, J = 1.6, 6.8 Hz, m-C_5H_4N, 2H), 7.07 (d, J = 5.6 Hz, m-C_5H_4N, 2H), 7.04 (d, J = 8.0 Hz, p-C_5H_4N, 2H). ^{13}C NMR (dmso-d_6): 207.7 (Fe-C), 153.8, 150.7, 150.0, 149.3, 140.5, 139.6, 127.6, 124.5, 123.7, 119.8, 118.9, 112.5.

References

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Ⅳ. Crystallographic Data of 1-3 and 12-14

Table S1. Summary of X-ray crystallographic data for complexes **1-3 and 12-14**.

	1	**2**	**3**
Formula	$C_{16}H_{16}CuF_{12}N_8O_2P_2$	$C_{16}H_{16}CuF_6N_8P$	$C_{39}H_{30}Cu_3F_{18}N_{12}P_3$
Fw	705.85	528.88	1292.28
Crystal system	triclinic	monoclinic	triclinic
space group	*P*-1	*C*2/*m*	*P*-1
a, Å	6.8197(6)	25.351(2)	14.1414(17)
b, Å	8.5461(10)	6.8638(7)	14.2973(18)
c, Å	11.1542(13)	11.9093(11)	14.795(2)
α, deg.	101.646(2)	90	82.063(2)
β, deg.	106.212(2)	105.551(2)	62.2200(10)
γ, deg.	98.9490(10)	90	66.5580(10)
V, Å^3	595.66(11)	1996.4(3)	2424.0(5)
Z	1	4	2
D_{calcd}, Mg/m^3	1.968	1.760	1.771
no. of reflns collected	3078	5070	12803
no. of indep rflns (R(int))	2059 (0.0184)	1925 (0.0507)	8436 (0.0263)
goodness-of-fit on F^2	1.058	1.054	0.940
R ($I > 2\sigma I$)	0.0449, 0.1161	0.0638, 0.1789	0.0464, 0.1088
R (all data)	0.0547, 0.1253	0.0799, 0.1992	0.0854, 0.1242
	12	**13**	**14**
Formula	$C_{20}H_{22}F_{12}FeN_{10}P_2$	$C_{30}H_{26}F_{12}FeN_{10}P_2$	$C_{32}H_{29}F_{12}FeN_{11}P_2$
Fw	748.27	872.40	913.45

Crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	*Pbcn*	*P*-1
a, Å	14.1189(14)	12.9083(13)	9.6742(11)
b, Å	17.770(2)	17.3384(17)	12.6282(14)
c, Å	12.6099(13)	15.1390(15)	17.4053(18)
α, deg.	90	90	99.9380(10)
β, deg.	105.422(2)	90	100.8340(10)
γ, deg.	90	90	110.391(2)
V, Å3	3049.8(6)	3388.2(6)	1891.0(4)
Z	4	4	2
D_{calcd}, Mg/m^3	1.630	1.710	1.604
no. of reflns collected	15160	13113	9671
no. of indep rflns (R(int))	5360 (0.0360)	2981(0.0840)	6505 (0.0383)
Goodness-of-fit on F^2	1.023	1.106	1.655
R ($I > 2\sigma I$)	0.0695, 0.1834	0.1025, 0.2595	0.1462, 0.4510
R (all data)	0.1104, 0.2239	0.1753, 0.3670	0.2030, 0.4820

V. The Crystal Structures of Compounds **1-3** and **12-14**

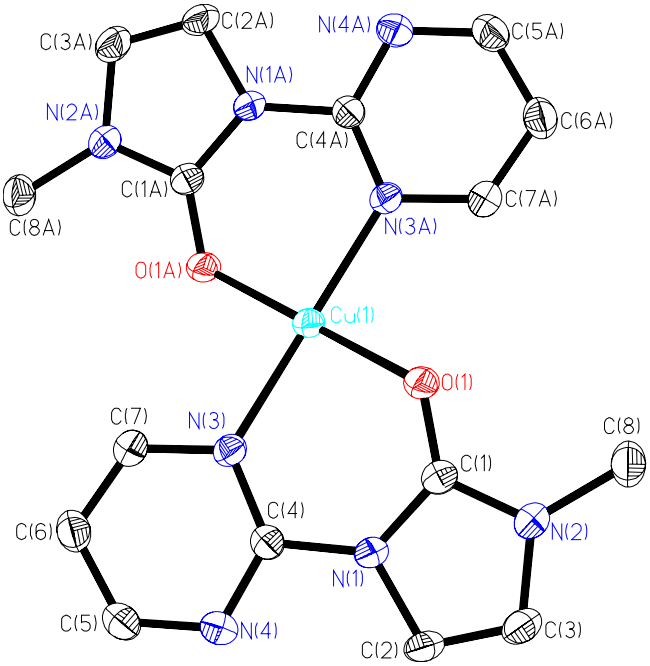

Figure S1. Molecular structure of the cation of **1**. Selected bond distances (Å) and angles (deg): Cu(1)-O(1) 1.900(2), Cu(1)-N(3) 2.042(3), O(1)#1-Cu(1)-O(1) 180.0, O(1)#1-Cu(1)-N(3) 90.21(11), O(1)-Cu(1)-N(3) 89.79(11), N(3)-Cu(1)-N(3)#1 180.0. Symmetry code: #1 -x+2,-y+1,-z+1.

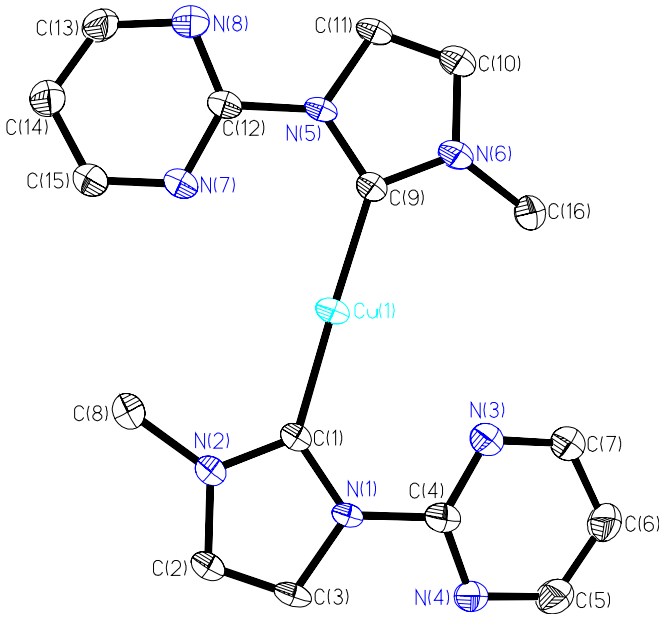

Figure S2. Molecular structure of the cation of **2**. Selected bond distances (Å) and angles (deg): Cu(1)-C(9) 1.914(7), Cu(1)-C(1) 1.916(6), C(9)-Cu(1)-C(1) 178.6(3). Symmetry

code: #1 x,-y+1,z.

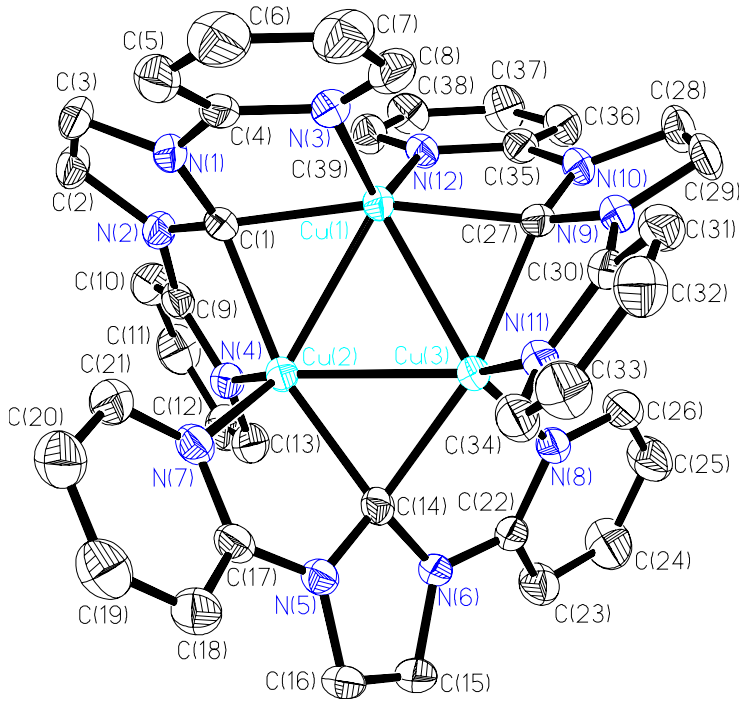

Figure S3. Molecular structure of the cation of **3**. Selected bond distances (Å) and angles (deg): Cu(1)-C(1) 2.033(5), Cu(1)-C(27) 2.040(4), Cu(1)-N(12) 2.071(4), Cu(1)-N(3) 2.088(4), Cu(1)-Cu(3) 2.4932(8), Cu(1)-Cu(2) 2.4971(8), Cu(2)-N(7) 2.057(4), Cu(2)-N(4) 2.065(4), Cu(2)-C(1) 2.076(4), Cu(2)-C(14) 2.083(4), Cu(2)-Cu(3) 2.4654(8), Cu(3)-N(8) 2.067(4), Cu(3)-N(11) 2.072(4), Cu(3)-C(14) 2.076(4), Cu(3)-C(27) 2.099(4), C(1)-Cu(1)-C(27) 166.44(17), C(1)-Cu(1)-N(12) 104.58(18), C(27)-Cu(1)-N(12) 82.06(17), C(1)-Cu(1)-N(3) 82.17(18), C(27)-Cu(1)-N(3) 103.50(18), N(12)-Cu(1)-N(3) 126.91(15), C(1)-Cu(1)-Cu(3) 112.39(13), C(27)-Cu(1)-Cu(3) 54.05(12), N(12)-Cu(1)-Cu(3) 109.39(11), N(3)-Cu(1)-Cu(3) 116.26(11), C(1)-Cu(1)-Cu(2) 53.37(13), C(27)-Cu(1)-Cu(2) 113.11(12), N(12)-Cu(1)-Cu(2) 117.44(11), N(3)-Cu(1)-Cu(2) 108.59(11), Cu(3)-Cu(1)-Cu(2) 59.21(2), N(7)-Cu(2)-N(4) 120.30(15), N(7)-Cu(2)-C(1) 103.91(17), N(4)-Cu(2)-C(1) 81.07(18), N(7)-Cu(2)-C(14) 82.01(17), N(4)-Cu(2)-C(14) 107.80(17), C(1)-Cu(2)-C(14) 165.34(18), N(7)-Cu(2)-Cu(3) 109.99(11), N(4)-Cu(2)-Cu(3) 123.12(11), C(1)-Cu(2)-Cu(3) 111.92(13), C(14)-Cu(2)-Cu(3) 53.52(12), N(7)-Cu(2)-Cu(1) 124.86(12), N(4)-Cu(2)-Cu(1) 104.98(11), C(1)-Cu(2)-Cu(1) 51.80(12), C(14)-Cu(2)-Cu(1) 113.79(12),

Cu(3)-Cu(2)-Cu(1) 60.31(2), N(8)-Cu(3)-N(11) 120.98(15), N(8)-Cu(3)-C(14) 82.85(17), N(11)-Cu(3)-C(14) 110.05(17), N(8)-Cu(3)-C(27) 100.02(16), N(11)-Cu(3)-C(27) 81.41(17), C(14)-Cu(3)-C(27) 164.83(17), N(8)-Cu(3)-Cu(2) 113.57(11), N(11)-Cu(3)-Cu(2) 120.17(11), C(14)-Cu(3)-Cu(2) 53.78(12), C(27)-Cu(3)-Cu(2) 112.20(12), N(8)-Cu(3)-Cu(1) 123.66(11), N(11)-Cu(3)-Cu(1) 103.42(11), C(14)-Cu(3)-Cu(1) 114.21(12), C(27)-Cu(3)-Cu(1) 51.88(12), Cu(2)-Cu(3)-Cu(1) 60.47(2).

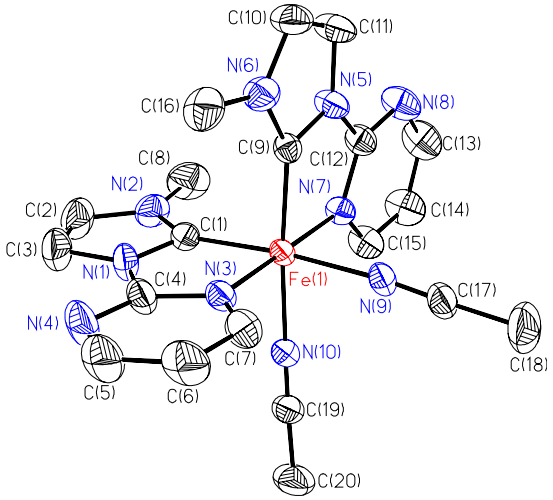

Figure S4. Molecular structure of the cation of **12**. Selected bond distances (Å) and angles (deg): Fe(1)-C(1) 1.908(6), Fe(1)-C(9) 1.909(5), Fe(1)-N(10) 1.976(5), Fe(1)-N(3) 1.978(5), Fe(1)-N(9) 1.979(5), Fe(1)-N(7) 1.989(4), C(1)-Fe(1)-C(9) 91.0(2), C(1)-Fe(1)-N(10) 91.4(2), C(9)-Fe(1)-N(10) 173.8(2), C(1)-Fe(1)-N(3) 81.5(2), C(9)-Fe(1)-N(3) 97.2(2), N(10)-Fe(1)-N(3) 88.78(19), C(1)-Fe(1)-N(9) 173.3(2), C(9)-Fe(1)-N(9) 92.2(2), N(10)-Fe(1)-N(9) 86.0(2), N(3)-Fe(1)-N(9) 92.2(2), C(1)-Fe(1)-N(7) 99.8(2), C(9)-Fe(1)-N(7) 81.2(2), N(10)-Fe(1)-N(7) 92.75(18), N(3)-Fe(1)-N(7) 177.94(19), N(9)-Fe(1)-N(7) 86.50(19).

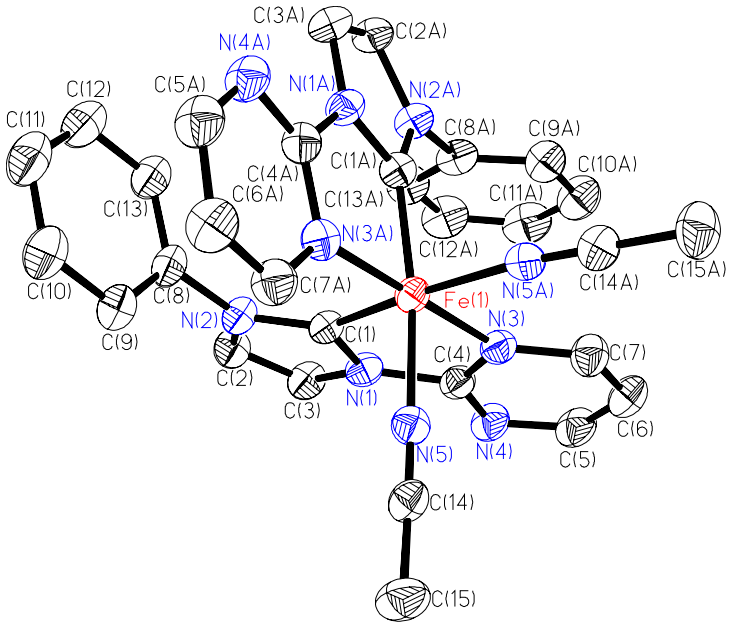

Figure S5. Molecular structure of the cation of **13**. Selected bond distances (Å) and angles (deg): Fe(1)-C(1) 1.908(9), Fe(1)-N(5) 1.976(9), Fe(1)-N(3) 2.008(8), C(1A)-Fe(1)-C(1) 85.2(5), C(1A)-Fe(1)-N(5) 171.1(3), C(1)-Fe(1)-N(5) 94.6(3), C(1A) -Fe(1)-N(5A) 94.6(3), C(1)-Fe(1)-N(5A) 171.1(3), N(5)-Fe(1)-N(5A) 87.1(4), C(1A)-Fe(1)-N(3) 100.9(3), C(1)-Fe(1)-N(3) 80.5(3), N(5)-Fe(1)-N(3) 87.8(3), N(5A)-Fe(1)-N(3) 90.8(3), C(1)-Fe(1)-N(3A) 100.9(3), N(5)-Fe(1)-N(3A) 90.8(3), Symmetry code: #1 -*x*+1, *y*, -*z*+1/2.

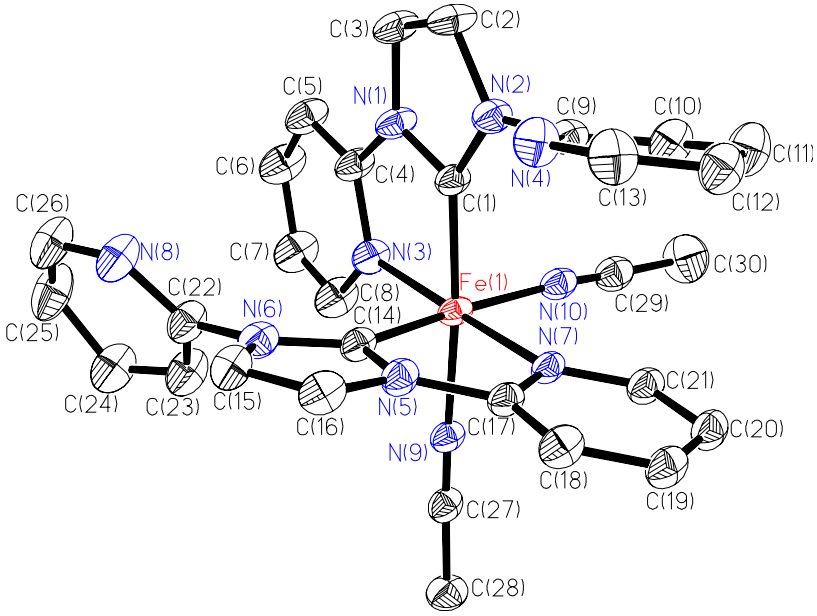

Figure S6. Molecular structure of the cation of **14**. Selected bond distances (Å) and angles (deg): Fe(1)-C(1) 1.903(12), Fe(1)-C(14) 1.939(15), Fe(1)-N(10) 1.971(14), Fe(1)-N(9)

1.972(10), Fe(1)-N(3) 1.987(11), Fe(1)-N(7) 1.988(9), C(1)-Fe(1)-C(14) 87.9(6), C(1)-Fe(1)-N(10) 92.0(5), C(14)-Fe(1)-N(10) 172.9(5), C(1)-Fe(1)-N(9) 173.6(5), C(14)-Fe(1)-N(9) 92.8(5), N(10)-Fe(1)-N(9) 88.0(5), C(1)-Fe(1)-N(3) 81.0(5), C(14)-Fe(1)-N(3) 99.2(5), N(10)-Fe(1)-N(3) 87.9(5), N(9)-Fe(1)-N(3) 92.6(4), C(1)-Fe(1)-N(7) 97.8(4), C(14)-Fe(1)-N(7) 81.0(5), N(10)-Fe(1)-N(7) 92.0(5), N(9)-Fe(1)-N(7) 88.7(4), N(3)-Fe(1)-N(7) 178.7(4). Symmetry code: #1 -x+1,-y+1,-z+2, #2 -x+2,-y+1,-z+1.