Electronic Supplementary Information (ESI)

Remarkable stability of copper(II)-N-heterocyclic carbene complexes void of an anionic tether

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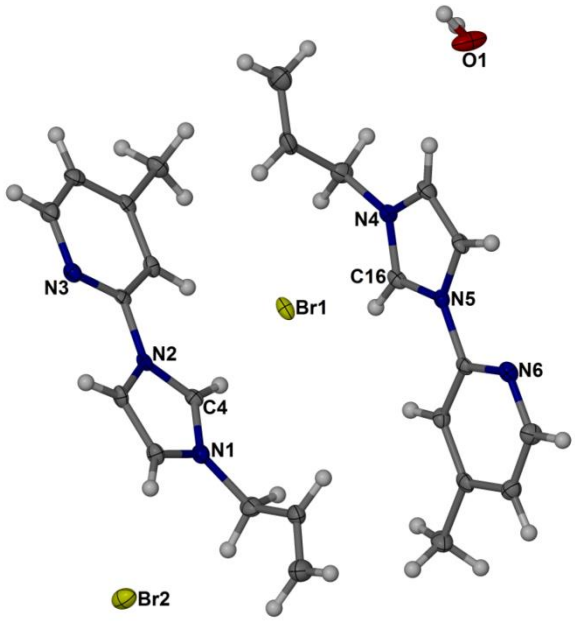
Contents

1. Modified synthetic procedure for imidazolium salt 1f[1]

1-Mesityl-3-(2-pyridyl)imidazolium bromide (**1f**). To a small round-bottomed flask was added 1-mesitylimidazole (1.1 g, 5.8 mmol) and 2-bromopyridine (0.58 ml, 6.0 mmol). The flask was sealed, fully submerged in silicone oil and the mixture was heated at 160°C with stirring for 10 hours. After this time, the solid formed was collected and washed with diethyl ether. Recrystallization from chloroform / diethyl ether gave the pure product as an off-white microcrystalline solid. Yield: 1.8 g, 5.3 mmol, 91 %. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.45 (s, 1H, NC*H*N), 9.25 (d, *J* = 7.7 Hz, 1H, py*H*), 8.91 (t, *J* = 1.8 Hz, 1H, im*H*), 8.53 (dd, *J* = 4.8, 1.4 Hz, 1H, py*H*), 8.11 (td, *J* = 7.7, 1.4 Hz, 1H, py*H*), 7.49 (dd, *J* = 7.7, 4.8 Hz, 1H, py*H*), 7.33 (t, *J* = 1.8 Hz, 1H, im*H*), 7.05 (s, 2H, mes*H*), 2.35 (s, 3H, p-CH_3), 2.19 (s, 6H, o-CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.8, 146.1, 141.8, 141.1, 136.4, 134.2, 130.7, 130.2, 125.7, 123.9, 120.2, 116.7, 21.3, 18.0. HRMS (ESI^+) m/z 264.1496 $[M - Br]^+$. Calculated $[M - Br]^+$ 264.1495. Anal. Calcd for $C_{17}H_{18}BrN_3$: C, 59.31; H, 5.27; N, 12.21. Found: C, 59.45; H, 5.25; N, 12.35.

2. Crystallographic data

1-Allyl-3-(2-(4-methylpyridyl)imidazolium bromide (1c)

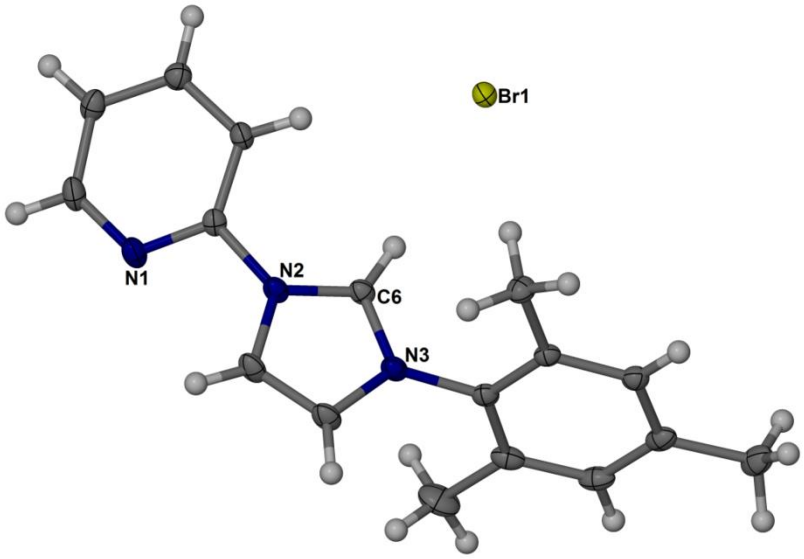


Crystal data and structure refinement.

Identification code	Ligand1c	
Formula	$C_{24}H_{30}Br_2N_6O$	
Formula weight	578.36	
Size	0.22 x 0.1 x 0.03 mm	
Crystal morphology	Colourless plate	
Temperature	100(2) K	
Wavelength	0.7107 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 5.1607(3) Å	α = 103.232(6)°
	b = 14.5382(10) Å	β = 98.132(5)°
	c = 18.2175(13) Å	γ = 99.232(5)°
Volume	1290.51(15) $Å^3$	
Z	2	
Density (calculated)	1.488 Mg/m^3	

Absorption coefficient	3.168 mm^{-1}
F(000)	588
Data collection range	$1.47 \leq \theta \leq 26.37°$
Index ranges	$-6 \leq h \leq 6$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$
Reflections collected	20313
Independent reflections	5293 [*R*(int) = 0.072]
Observed reflections	4332 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	1 and 0.55863
Refinement method	Full
Data / restraints / parameters	5293 / 0 / 308
Goodness of fit	1.056
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0354$, $wR_2 = 0.0727$
R indices (all data)	$R_1 = 0.0485$, $wR_2 = 0.0801$
Largest diff. peak and hole	0.673 and -0.648e.$Å^{-3}$

1-Mesityl-3-(2-pyridyl)imidazolium bromide (**1f**)

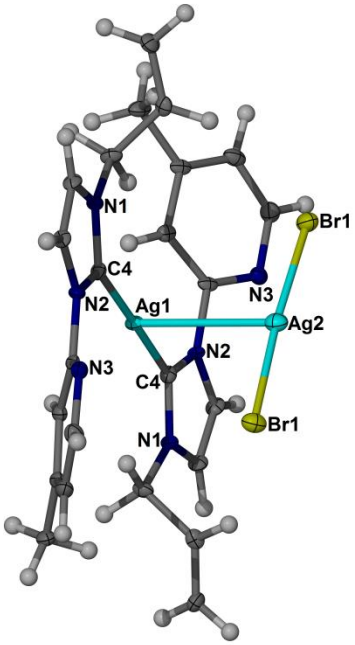


Crystal data and structure refinement.

Identification code	Ligand1f
Formula	$C_{17}H_{18}BrN_3$

Formula weight	344.25
Size	0.44 x 0.26 x 0.06 mm
Crystal morphology	Colourless plate
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.8130(9) Å α = 90°
	b = 13.5394(10) Å β = 100.192(4)°
	c = 12.4616(10) Å γ = 90°
Volume	1629.5(2) $Å^3$
Z	4
Density (calculated)	1.403 Mg/m^3
Absorption coefficient	2.52 mm^{-1}
F(000)	704
Data collection range	$2.24 \leq \theta \leq 30.21°$
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-17 \leq l \leq 17$
Reflections collected	44614
Independent reflections	4838 [R(int) = 0.0307]
Observed reflections	4267 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.8635 and 0.4035
Refinement method	Full
Data / restraints / parameters	4838 / 0 / 193
Goodness of fit	1.06
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0222, wR_2 = 0.056
R indices (all data)	R_1 = 0.0273, wR_2 = 0.0576
Largest diff. peak and hole	0.529 and -0.405e.$Å^{-3}$

Bis[1-allyl-3-(2-(4-methyl)pyridyl)imidazol-2-ylidene] silver(I) silver dibromide (2c)

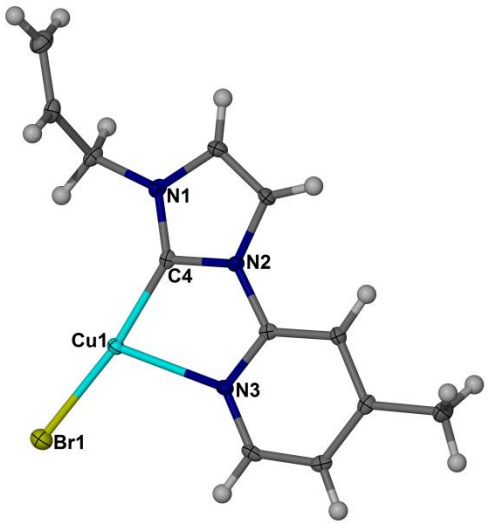


Crystal data and structure refinement.

Identification code	Complex2c	
Formula	$C_{24}H_{26}Ag_2Br_2N_6$	
Formula weight	774.07	
Size	0.27 x 0.21 x 0.16 mm	
Crystal morphology	Colourless block	
Temperature	100.01(10) K	
Wavelength	0.7107 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 15.7608(7) Å	α = 90°
	b = 7.0808(3) Å	β = 96.190(4)°
	c = 23.1906(9) Å	γ = 90°
Volume	2572.96(19) $Å^3$	
Z	4	
Density (calculated)	1.998 Mg/m^3	
Absorption coefficient	4.653 mm^{-1}	
F(000)	1504	

Data collection range	$2.6 \leq \theta \leq 26.37°$
Index ranges	$-19 \leq h \leq 17$, $-8 \leq k \leq 5$, $-28 \leq l \leq 25$
Reflections collected	5090
Independent reflections	2607 [R(int) = 0.0326]
Observed reflections	2306 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.5231 and 0.3664
Refinement method	Full
Data / restraints / parameters	2607 / 0 / 156
Goodness of fit	1.045
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0302, wR_2 = 0.0619
R indices (all data)	R_1 = 0.0365, wR_2 = 0.0656
Largest diff. peak and hole	0.617 and -0.707e.Å^{-3}

[1-Allyl-3-(2-(4-methyl)pyridyl)imidazol-2-ylidene] copper(I) bromide (**3c**)

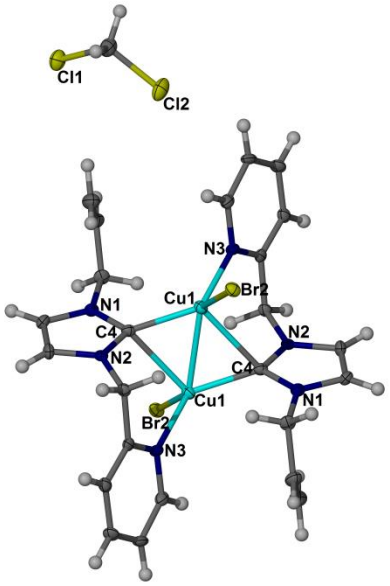


Crystal data and structure refinement.

Identification code	Complex3c
Formula	$C_{12}H_{13}BrCuN_3$
Formula weight	342.7
Size	0.21 x 0.16 x 0.11 mm

Crystal morphology	Yellow block
Temperature	100(2) K
Wavelength	0.7107 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 6.8081(8) Å α = 90°
	b = 13.4780(13) Å β = 92.591(9)°
	c = 13.8979(13) Å γ = 90°
Volume	1274.0(2) Å^3
Z	4
Density (calculated)	1.787 Mg/m^3
Absorption coefficient	4.831 mm^{-1}
F(000)	680
Data collection range	$2.11 \leq \theta \leq 25.68°$
Index ranges	$-6 \leq h \leq 8$, $-14 \leq k \leq 16$, $-16 \leq l \leq 15$
Reflections collected	5035
Independent reflections	2409 [R(int) = 0.0238]
Observed reflections	2138 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	1 and 0.78528
Refinement method	Full
Data / restraints / parameters	2409 / 0 / 155
Goodness of fit	1.065
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0372, wR_2 = 0.0923
R indices (all data)	R_1 = 0.0435, wR_2 = 0.096
Largest diff. peak and hole	0.73 and -0.913e.Å^{-3}

[1-Allyl-3-(2-methylpyridyl)imidazol-2-ylidene] copper(I) bromide (**3e**)

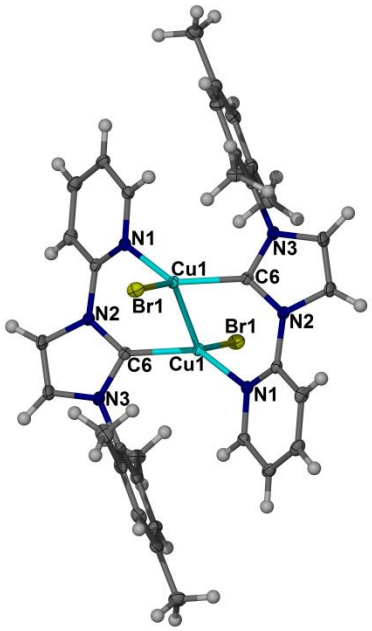


Crystal data and structure refinement.

Identification code	Complex3e	
Formula	$C_{26}H_{30}Br_2Cl_4Cu_2N_6$	
Formula weight	855.26	
Size	0.16 x 0.07 x 0.04 mm	
Crystal morphology	Yellow needle	
Temperature	99.96(14) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.7314(6) Å	α = 90°
	b = 8.2776(4) Å	β = 100.032(5)°
	c = 16.4014(7) Å	γ = 90°
Volume	1568.35(13) $Å^3$	
Z	2	
Density (calculated)	1.811 Mg/m^3	
Absorption coefficient	4.273 mm^{-1}	
F(000)	848	
Data collection range	$3.4 \leq \theta \leq 28.28°$	
Index ranges	$-15 \leq h \leq 10$, $-8 \leq k \leq 10$, $-21 \leq l \leq 19$	

Reflections collected	7234
Independent reflections	3852 [*R*(int) = 0.044]
Observed reflections	3003 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.8477 and 0.548
Refinement method	Full
Data / restraints / parameters	3852 / 0 / 181
Goodness of fit	1.035
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0429$, $wR_2 = 0.0839$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.0937$
Largest diff. peak and hole	0.963 and -0.629e.Å^{-3}

[1-Mesityl-3-(2-pyridyl)imidazol-2-ylidene] copper(I) bromide (3f)

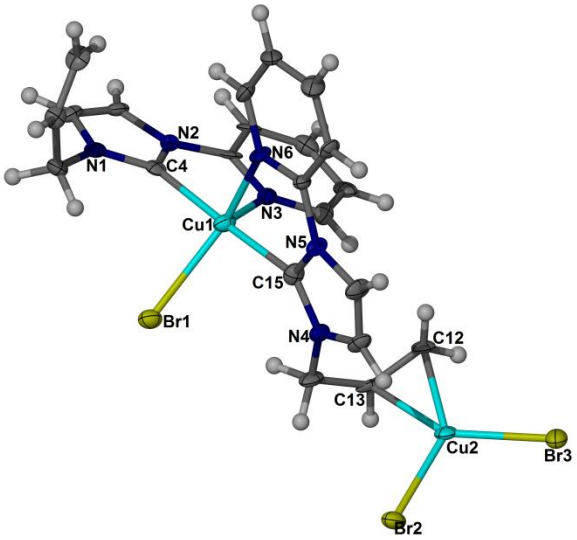


Crystal data and structure refinement.

Identification code	Complex3f
Formula	$C_{34}H_{34}Br_2Cu_2N_6$
Formula weight	813.57
Size	0.35 x 0.14 x 0.07 mm
Crystal morphology	Yellow fragment
Temperature	120(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.7104(5) Å	α = 90°
	b = 11.0398(6) Å	β = 104.0190(10)°
	c = 15.3078(8) Å	γ = 90°
Volume	1592.13(15) Å^3	
Z	2	
Density (calculated)	1.697 Mg/m^3	
Absorption coefficient	3.88 mm^{-1}	
F(000)	816	
Data collection range	$2.3 \leq \theta \leq 31.64°$	
Index ranges	$-14 \leq h \leq 7$, $-15 \leq k \leq 16$, $-22 \leq l \leq 20$	
Reflections collected	14966	
Independent reflections	5099 [R(int) = 0.0307]	
Observed reflections	4033 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7729 and 0.3437	
Refinement method	Full	
Data / restraints / parameters	5099 / 0 / 202	
Goodness of fit	1.046	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0285, wR_2 = 0.063	
R indices (all data)	R_1 = 0.0438, wR_2 = 0.0672	
Largest diff. peak and hole	0.503 and -0.521e.Å^{-3}	

Upon exposure to low oxygen levels, complex 3b oxidises to give complex 4b'.

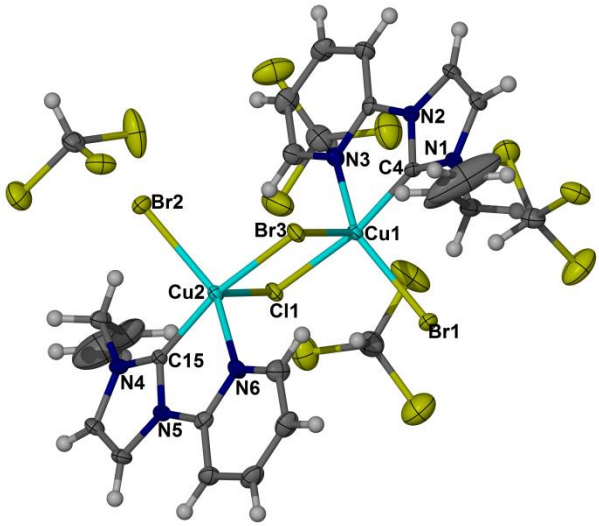


Crystal data and structure refinement.

Identification code	Complex4b'	
Formula	$C_{22}H_{22}Br_3Cu_2N_6$	
Formula weight	737.27	
Size	0.13 x 0.05 x 0.02 mm	
Crystal morphology	Green needle	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 7.3691(10) Å	α = 84.446(5)°
	b = 11.7443(14) Å	β = 87.611(5)°
	c = 14.3091(19) Å	γ = 89.928(5)°
Volume	1231.5(3) $Å^3$	
Z	2	
Density (calculated)	1.988 Mg/m^3	
Absorption coefficient	6.617 mm^{-1}	
F(000)	718	
Data collection range	$1.74 \le \theta \le 20.84°$	
Index ranges	$-7 \le h \le 7,\ -11 \le k \le 11,\ -14 \le l \le 14$	
Reflections collected	9479	

Independent reflections	2554 [R(int) = 0.0613]
Observed reflections	1934 [I >2σ(I)]
Absorption correction	multi-scan
Max. and min. transmission	0.879 and 0.48
Refinement method	Full
Data / restraints / parameters	2554 / 0 / 292
Goodness of fit	1.013
Final R indices [I >2σ(I)]	R_1 = 0.0443, wR_2 = 0.0958
R indices (all data)	R_1 = 0.0684, wR_2 = 0.1054
Largest diff. peak and hole	0.656 and -0.711e.Å^{-3}

Upon exposure to air, complex 3b oxidises to give complex 4b.

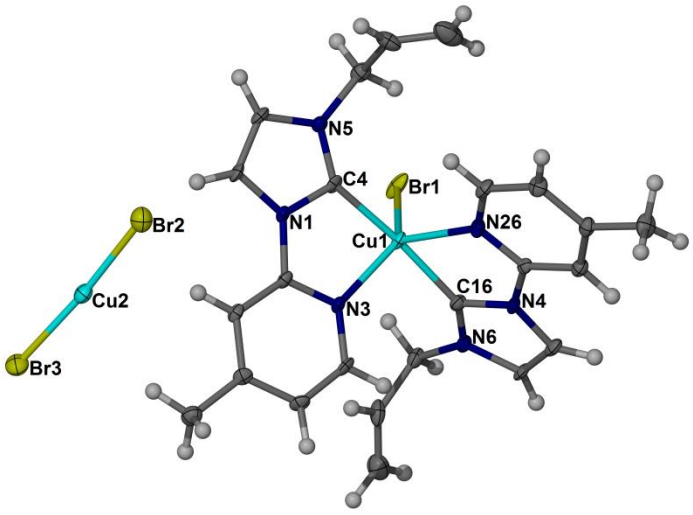


Crystal data and structure refinement.

Identification code	Complex4b
Formula	$C_{26}H_{26}Br_{2.40}Cl_{13.60}Cu_2N_6$
Formula weight	1223.51
Size	0.37 x 0.05 x 0.03 mm
Crystal morphology	Green needle
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$

Unit cell dimensions	a = 20.8642(10) Å	α = 90°
	b = 8.9422(4) Å	β = 90.963(2)°
	c = 23.5483(10) Å	γ = 90°
Volume	4392.8(3) Å^3	
Z	4	
Density (calculated)	1.85 Mg/m^3	
Absorption coefficient	4.008 mm^{-1}	
F(000)	2389	
Data collection range	$2 \leq \theta \leq 29.56°$	
Index ranges	$-27 \leq h \leq 28$, $-12 \leq k \leq 8$, $-32 \leq l \leq 32$	
Reflections collected	38524	
Independent reflections	12245 [R(int) = 0.0573]	
Observed reflections	7002 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.8892 and 0.3186	
Refinement method	Full	
Data / restraints / parameters	12245 / 2 / 451	
Goodness of fit	1.022	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0599, wR_2 = 0.1404	
R indices (all data)	R_1 = 0.1205, wR_2 = 0.1672	
Largest diff. peak and hole	2.545 and -1.385e.Å^{-3}	

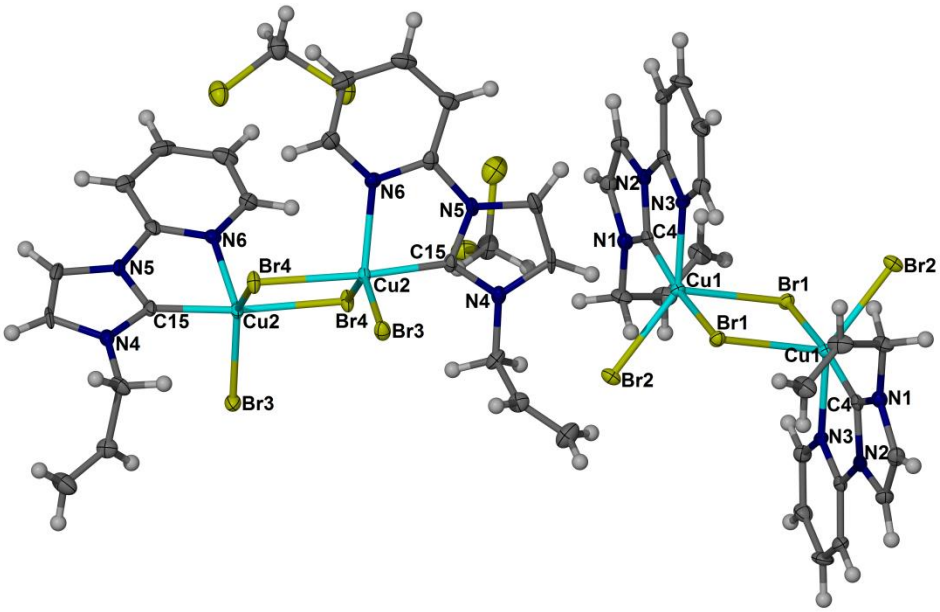
Upon exposure to air, complex 3c oxidises to give complex 4c'.



Crystal data and structure refinement.

Identification code	Complex3c’	
Formula	$C_{24}H_{26}Br_3Cu_2N_6$	
Formula weight	765.32	
Size	0.23 x 0.07 x 0.03 mm	
Crystal morphology	Blue fragment	
Temperature	100.01(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.6616(6) Å	α = 90°
	b = 12.1029(4) Å	β = 102.622(4)°
	c = 15.9899(6) Å	γ = 90°
Volume	2768.80(18) $Å^3$	
Z	4	
Density (calculated)	1.836 Mg/m^3	
Absorption coefficient	5.89 mm^{-1}	
F(000)	1500	
Data collection range	$1.71 \leq \theta \leq 28.28°$	
Index ranges	$-19 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 21$	
Reflections collected	12551	
Independent reflections	6821 [R(int) = 0.0349]	
Observed reflections	4706 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.8431 and 0.3444	
Refinement method	Full	
Data / restraints / parameters	6821 / 0 / 318	
Goodness of fit	1.034	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0577, wR_2 = 0.1433	
R indices (all data)	R_1 = 0.0943, wR_2 = 0.1661	
Largest diff. peak and hole	1.342 and -2.468e.$Å^{-3}$	

Cu(NHC)Br_2 (5b)

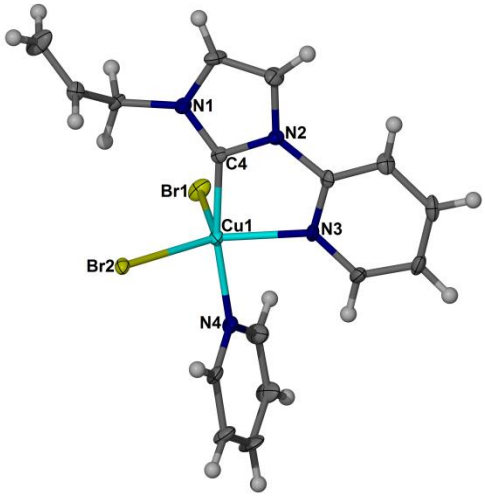


Crystal data and structure refinement.

Identification code	Complex5b	
Formula	$C_{47}H_{50}Br_8Cl_6Cu_4N_{12}$	
Formula weight	1889.09	
Size	0.14 x 0.1 x 0.08 mm	
Crystal morphology	Dark green block	
Temperature	100.0(3) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 30.804(2) Å	α = 90°
	b = 9.2483(6) Å	β = 98.203(6)°
	c = 21.9433(12) Å	γ = 90°
Volume	6187.4(7) $Å^3$	
Z	4	
Density (calculated)	2.028 Mg/m^3	
Absorption coefficient	6.826 mm^{-1}	
F(000)	3656	
Data collection range	3.21 ≤ θ ≤ 28.28°	
Index ranges	-31 ≤ *h* ≤40, -9 ≤ *k* ≤ 12, -27 ≤ *l* ≤ 29	

Reflections collected	15480
Independent reflections	7609 [*R*(int) = 0.0412]
Observed reflections	5663 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.6112 and 0.4483
Refinement method	Full
Data / restraints / parameters	7609 / 0 / 348
Goodness of fit	1.059
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.087$
R indices (all data)	$R_1 = 0.0705$, $wR_2 = 0.0959$
Largest diff. peak and hole	0.98 and -0.659e.Å^{-3}

Cu(NHC)Br$_2$(pyridine) (5b·pyridine)

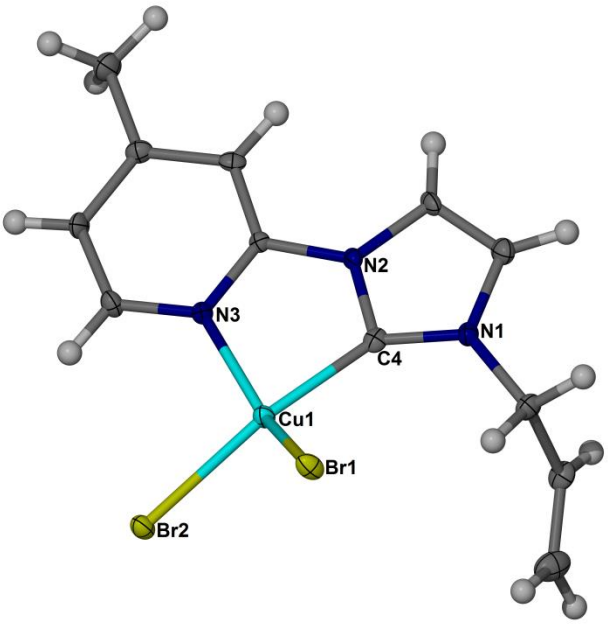


Crystal data and structure refinement.

Identification code	Complex5b-pyr
Formula	$C_{16}H_{16}Br_2CuN_4$
Formula weight	487.69
Size	0.42 x 0.27 x 0.24 mm
Crystal morphology	Green polyhedron
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$P3_121$

Unit cell dimensions	a = 11.8735(5) Å α = 90°
	b = 11.8735(5) Å β = 90°
	c = 21.5549(10) Å γ = 120°
Volume	2631.7(2) Å^3
Z	6
Density (calculated)	1.846 Mg/m^3
Absorption coefficient	5.803 mm^{-1}
F(000)	1434
Data collection range	$3.43 \leq \theta \leq 28.24°$
Index ranges	$-11 \leq h \leq 15$, $-15 \leq k \leq 9$, $-16 \leq l \leq 28$
Reflections collected	7357
Independent reflections	4256 [R(int) = 0.0351]
Observed reflections	3909 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.3365 and 0.1943
Refinement method	Full
Data / restraints / parameters	4256 / 0 / 208
Goodness of fit	1.03
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0336, wR_2 = 0.0582
R indices (all data)	R_1 = 0.0398, wR_2 = 0.061
Largest diff. peak and hole	0.397 and -0.448e.Å^{-3}
Absolute structure parameter	0.004(10)

Cu(NHC)Br_2 (5c)

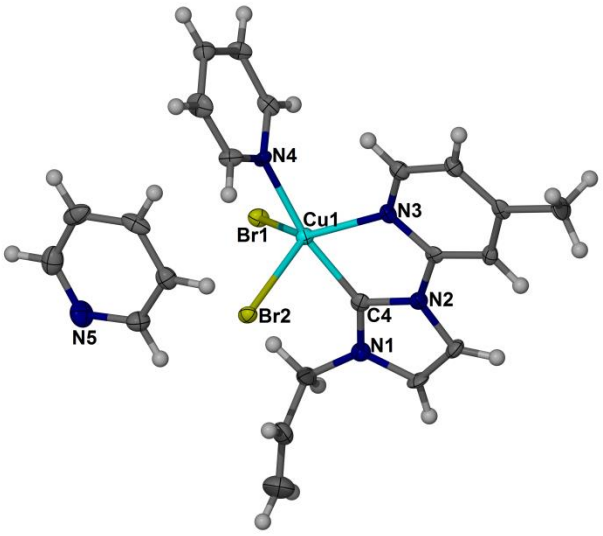


Crystal data and structure refinement.

Identification code	Complex5c	
Formula	$C_{12}H_{13}Br_2CuN_3$	
Formula weight	422.61	
Size	0.3 x 0.14 x 0.13 mm	
Crystal morphology	Dark green block	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.2410(3) Å	α = 90°
	b = 13.9377(5) Å	β = 95.114(3)°
	c = 12.2518(4) Å	γ = 90°
Volume	1401.65(9) $Å^3$	
Z	4	
Density (calculated)	2.003 Mg/m^3	
Absorption coefficient	7.244 mm^{-1}	
F(000)	820	
Data collection range	$3.37 \leq \theta \leq 28.28°$	

Index ranges	$-8 \le h \le 10$, $-18 \le k \le 16$, $-16 \le l \le 12$
Reflections collected	6431
Independent reflections	3458 [R(int) = 0.0339]
Observed reflections	2854 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.4527 and 0.2198
Refinement method	Full
Data / restraints / parameters	3458 / 0 / 164
Goodness of fit	1.036
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0356, wR_2 = 0.0643
R indices (all data)	R_1 = 0.0483, wR_2 = 0.0703
Largest diff. peak and hole	0.656 and -0.63e.Å^{-3}

Cu(NHC)Br$_2$(pyridine) (5c·pyridine)

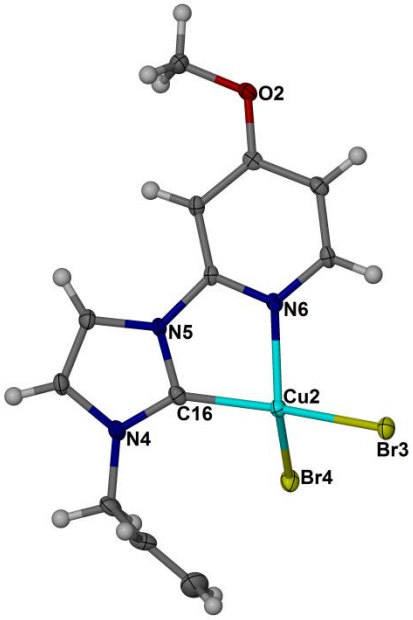


Crystal data and structure refinement.

Identification code	Complex5c-pyr
Formula	$C_{22}H_{23}Br_2CuN_5$
Formula weight	580.81
Size	0.21 x 0.14 x 0.06 mm
Crystal morphology	Green plate
Temperature	100.0(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.4531(8) Å	α = 90°
	b = 11.7823(9) Å	β = 93.976(7)°
	c = 15.7477(18) Å	γ = 90°
Volume	2305.0(3) Å^3	
Z	4	
Density (calculated)	1.674 Mg/m^3	
Absorption coefficient	4.433 mm^{-1}	
F(000)	1156	
Data collection range	$2.97 \leq \theta \leq 26.37°$	
Index ranges	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-13 \leq l \leq 19$	
Reflections collected	9260	
Independent reflections	4691 [R(int) = 0.0488]	
Observed reflections	3340 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.7768 and 0.4562	
Refinement method	Full	
Data / restraints / parameters	4691 / 0 / 272	
Goodness of fit	1.005	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0442, wR_2 = 0.075	
R indices (all data)	R_1 = 0.0781, wR_2 = 0.0855	
Largest diff. peak and hole	0.683 and -0.63e.Å^{-3}	

Cu(NHC)Br_2 (5d)

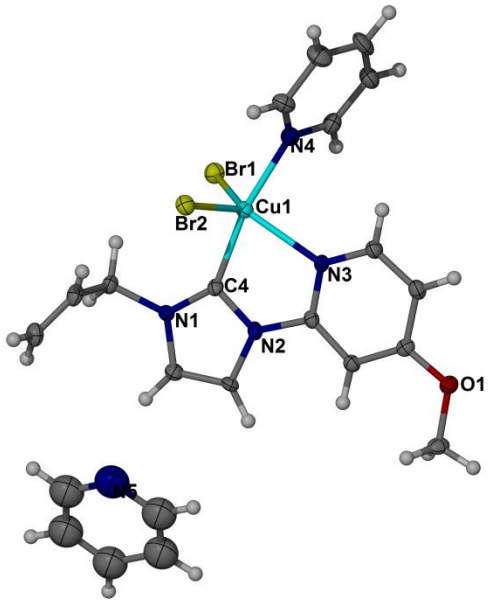


Crystal data and structure refinement.

Identification code	Complex5d	
Formula	$C_{12}H_{13}Br_2CuN_3O$	
Formula weight	438.61	
Size	0.06 x 0.06 x 0.04 mm	
Crystal morphology	Green block	
Temperature	100.0(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.8047(2) Å	α = 90°
	b = 12.1711(2) Å	β = 102.211(2)°
	c = 15.4734(3) Å	γ = 90°
Volume	1436.59(5) $Å^3$	
Z	4	
Density (calculated)	2.028 Mg/m^3	
Absorption coefficient	8.626 mm^{-1}	
F(000)	852	
Data collection range	$4.66 \leq \theta \leq 66.58°$	

Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-18 \le l \le 18$
Reflections collected	7410
Independent reflections	2526 [R(int) = 0.027]
Observed reflections	2333 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.7241 and 0.6256
Refinement method	Full
Data / restraints / parameters	2526 / 0 / 173
Goodness of fit	1.035
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0204, wR_2 = 0.0468
R indices (all data)	R_1 = 0.0235, wR_2 = 0.0484
Largest diff. peak and hole	0.372 and -0.392e.Å^{-3}

Cu(NHC)Br$_2$(pyridine) (5d·pyridine)

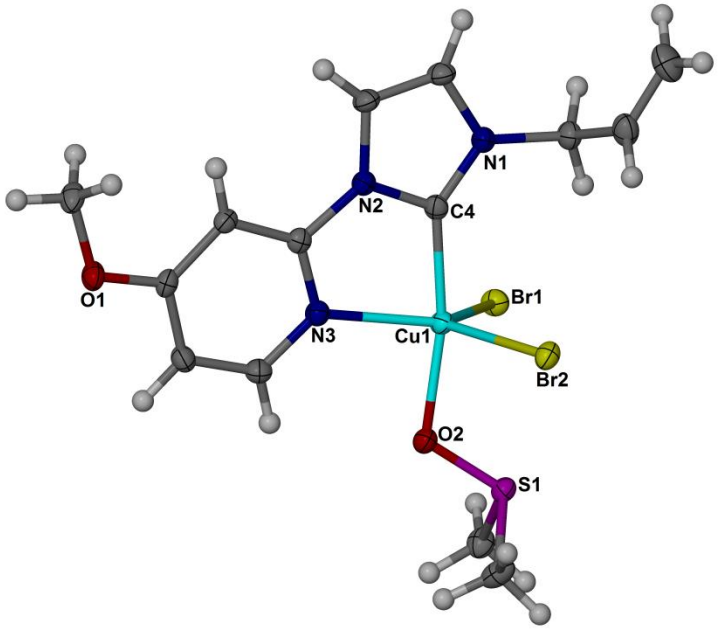


Crystal data and structure refinement.

Identification code	Complex5d-pyr
Formula	$C_{22}H_{23}Br_2CuN_5O$
Formula weight	596.81
Size	0.14 x 0.05 x 0.03 mm
Crystal morphology	Green needle
Temperature	99.9(3) K

Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	$R\ \bar{3}$	
Unit cell dimensions	a = 36.5062(9) Å	α = 90°
	b = 36.5062(9) Å	β = 90°
	c = 10.6415(3) Å	γ = 120°
Volume	12281.9(6) $Å^3$	
Z	18	
Density (calculated)	1.452 Mg/m^3	
Absorption coefficient	4.724 mm^{-1}	
F(000)	5346	
Data collection range	$4.38 \leq \theta \leq 66.53°$	
Index ranges	$-40 \leq h \leq 40$, $-42 \leq k \leq 29$, $-12 \leq l \leq 12$	
Reflections collected	9288	
Independent reflections	4811 [R(int) = 0.0455]	
Observed reflections	3818 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.8713 and 0.5576	
Refinement method	Full	
Data / restraints / parameters	4811 / 0 / 251	
Goodness of fit	1.007	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0488, wR_2 = 0.1264	
R indices (all data)	R_1 = 0.0624, wR_2 = 0.1344	
Largest diff. peak and hole	0.961 and -0.835e.$Å^{-3}$	

Cu(NHC)Br_2·dmso (4d·dmso)

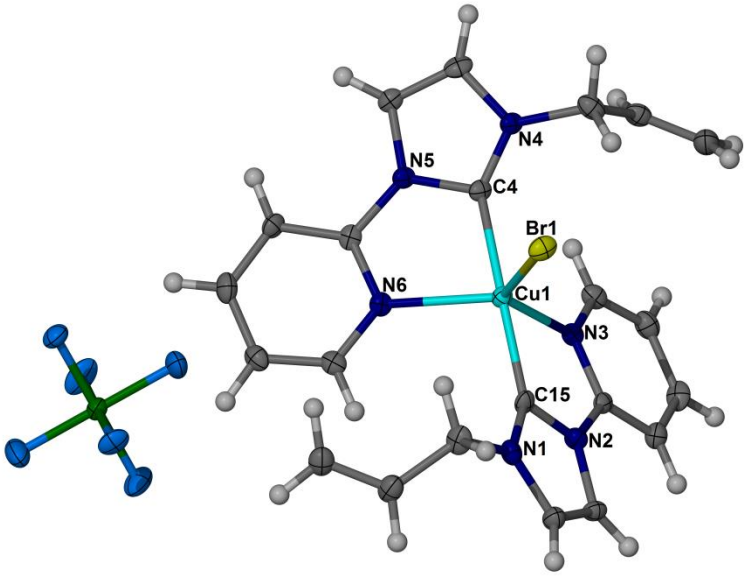


Crystal data and structure refinement.

Identification code	Complex5d-dmso	
Formula	$C_{33}H_{45}Br_4Cu_2N_6O_5S_2$	
Formula weight	1116.59	
Size	0.11 x 0.05 x 0.03 mm	
Crystal morphology	Blue needle	
Temperature	99.9(4) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 20.3292(7) Å	α = 90°
	b = 12.6548(3) Å	β = 102.552(3)°
	c = 17.0258(5) Å	γ = 90°
Volume	4275.4(2) $Å^3$	
Z	4	
Density (calculated)	1.735 Mg/m^3	
Absorption coefficient	6.889 mm^{-1}	
F(000)	2220	
Data collection range	$4.14 \leq \theta \leq 66.6°$	

Index ranges	$-24 \le h \le 19$, $-14 \le k \le 15$, $-11 \le l \le 20$
Reflections collected	8036
Independent reflections	3776 [R(int) = 0.0249]
Observed reflections	3292 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.82 and 0.5179
Refinement method	Full
Data / restraints / parameters	3776 / 5 / 232
Goodness of fit	1.05
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0392, wR_2 = 0.1064
R indices (all data)	R_1 = 0.046, wR_2 = 0.1125
Largest diff. peak and hole	1.66 and -1.523e.Å^{-3}

[Cu(NHC)2Br]PF6 (6b)

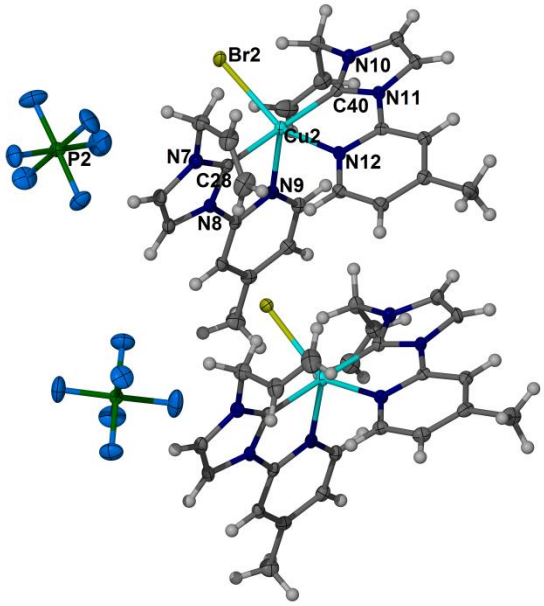


Crystal data and structure refinement.

Identification code	Complex6b
Formula	$C_{22}H_{22}BrCuF_6N_6P$
Formula weight	658.88
Size	0.06 x 0.03 x 0.02 mm
Crystal morphology	Blue fragment

Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 7.0531(2) Å	α = 89.147(4)°
	b = 13.1532(8) Å	β = 88.799(3)°
	c = 13.4067(5) Å	γ = 82.046(4)°
Volume	1231.42(9) Å^3	
Z	2	
Density (calculated)	1.777 Mg/m^3	
Absorption coefficient	4.412 mm^{-1}	
F(000)	658	
Data collection range	$3.3 \leq \theta \leq 66.6°$	
Index ranges	$-8 \leq h \leq 5$, $-14 \leq k \leq 15$, $-15 \leq l \leq 14$	
Reflections collected	8031	
Independent reflections	4205 [R(int) = 0.0424]	
Observed reflections	3370 [$I > 2\sigma(I)$]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9169 and 0.7777	
Refinement method	Full	
Data / restraints / parameters	4205 / 0 / 323	
Goodness of fit	1.161	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0706, wR_2 = 0.1848	
R indices (all data)	R_1 = 0.0875, wR_2 = 0.1917	
Largest diff. peak and hole	2.01 and -0.529e.Å^{-3}	

[Cu(NHC)2Br]PF6 (6c)



Crystal data and structure refinement.

Identification code	Complex6c	
Formula	$C_{24}H_{26}Br_1Cu_1F_6N_6P$	
Formula weight	686.93	
Size	0.23 x 0.12 x 0.05 mm	
Crystal morphology	Blue plate	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 13.2357(4) Å	α = 62.942(3)°
	b = 14.5874(4) Å	β = 89.791(2)°
	c = 15.6494(5) Å	γ = 88.691(2)°
Volume	2690.01(16) $Å^3$	
Z	4	
Density (calculated)	1.696 Mg/m^3	
Absorption coefficient	4.067 mm^{-1}	
F(000)	1380	
Data collection range	$3.17 \le \theta \le 66.6°$	
Index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-18 \le l \le 18$	

Reflections collected	56823
Independent reflections	9200 [R(int) = 0.0341]
Observed reflections	8168 [$I > 2\sigma(I)$]
Absorption correction	multi-scan
Max. and min. transmission	0.8225 and 0.4548
Refinement method	Full
Data / restraints / parameters	9200 / 0 / 707
Goodness of fit	1.017
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0312, wR_2 = 0.0837
R indices (all data)	R_1 = 0.0359, wR_2 = 0.0876
Largest diff. peak and hole	1.057 and -0.717e.Å^{-3}

1. B. R. M. Lake and C. E. Willans, *Chem.-Eur. J.*, 2013, **19**, 16780-16790.