Electronic Supplementary Information for Dalton Transactions

Dual reactivity of N-heterocyclic carbenes towards copper(II) salts

Eugene L. Kolychev,[a] Viacheslav V. Shuntikov,[b] Victor N. Khrustalev,[b] Alexander A. Bush[a,c] and Mikhail S. Nechaev[*,a,c]

[a]A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky Prosp., 29, Moscow 119991, Russian Federation, [b]A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Vavilov Str., 28, Moscow 119991, Russian Federation and [c]Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow 119991, Russian Federation

*Corresponding author. Fax: +7(495)9392677 E-mail: nechaev@nmr.chem.msu.ru

Supporting Information

1. Experimental details.

1.1 General information.

Unless otherwise stated, all manipulations were carried out using standard Schlenk technique under an argon atmosphere. Dichloromethane was distilled prior to use over CaH2 in argon atmosphere. Diethyl ether was distilled over sodium-benzophenone. Unsaturated amidinium precursors prepared by method published by Hintermann[1]. Free N-heterocyclic carbenes were prepared from corresponding amidinium salts by method published by Cavell et al.[2]. Silver complexes were prepared by methods we and Cavell et al. early reported[2]. Other chemicals and solvents were obtained from commercial sources and used without further purification. NMR spectra were obtained on a Bruker ‘‘Avance 400” (400 MHz ^{1}H, 101 MHz ^{13}C) and Bruker “Avance 600” (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to solvent peaks[3]. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ‘‘s”, ‘‘d”, or ‘‘m” for singlet, doublet, or multiplet, respectively. The abbreviation ‘‘br” is given for broadened signals. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer at the Institute of Petrochemical Synthesis, Russian Academy of Sciences.

1.3 General procedure of reaction silver complexes with copper(II) salts.

A mixture of silver complex (1 eq.) and copper salt (2 eq.) was dissolved in CH_2Cl_2 or $CHCl_3$ (approx. 0,02M). Mixture was stirred for 24 hours, filtered through short pad of Celite®, and evaporated to give mixture of Wanzlick salts with different anions. (If product was insoluble in CH_2Cl_2 or $CHCl_3$ reaction mixture was evaporated, redissolved, filtered through short pad of Celite®, and evaporated again).

[(6-Dipp)Br]X

^{1}H NMR(DMSO-d_6, 400 MHz, δ, ppm): 7.41-7.50 (m, 2H, Ar-Dipp-H); 7.37 (d, J = 6.1, 4H, Ar-Dipp-H); 4.05 (br.s, 4H, CH_2-N); 2.83 (br.s, 4H, iPr); 2.45 (br.s, 2H, CH_2); 1.25 (d, J = 5.4, 12H, iPr); 1.19 (d, J = 5.6; 12H, iPr).

^{13}C NMR(DMSO-d_6, 101 MHz, δ, ppm): 148.5 (C-Br); 142.1 (Ar); 136.6 (Ar); 129.0 (Ar); 123.6 (Ar); 50.4 (N-CH_2) 26.5 (iPr); 22.9 (iPr) 21.5 (CH_2)

[(7-Dipp)Br]X

^{1}H NMR(DMSO-d_6, 400 MHz, δ, ppm): 7.46-7.53 (m, 2H, Ar-Dipp-H); 7.42 (d, J = 7.6, 4H, Ar-Dipp-H); 4.44 (br. s, 4H, CH_2-N); 2.93 (dt, J = 12.7, 6.1, 4H, iPr); 2.33 (br.s, 4H, CH_2); 1.34 (d, J = 6.6, 12H, iPr); 1.25 (d, J = 6.6; 12H, iPr).

^{13}C NMR(DMSO-d_6, 101 MHz, δ, ppm): 154.3 (C-Br); 142.6 (Ar); 130.1 (Ar); 125.1 (Ar); 57.0 (N-CH2); 28.1 (iPr); 23.8 (iPr); 22.9 (iPr); 22.3 (CH_2).

4.4 General procedure for synthesis of pure bromoamidinium salts.

To the solution of silver complex in CH_2Cl_2 (approx. 0,02M) 1M solution of bromine in CH_2Cl_2 (1 eq) was added. Color of mixture turned to yellow, and some amount AgBr was precipitated. At this stage an aliquot of solution was evaporated and analyzed by NMR. Analysis shows that the solution contains a mixture of bromoamidinium salt and starting material. We explain this fact by formation of Br_3^- anions, which can react more slowly. Reaction mixture was allowed to stand at 48 h in dark place. Mixture became colorless, and an additional amount of AgBr was precipitated. Mixture was filtered through a short pad of Celite® and evaporated to dryness to give the pure target product.

[(IPr)Br]Br

Yield: 0.493 g (92%), white powder.

^{1}H NMR(DMSO-d_6, 600 MHz, δ, ppm): 8.88 (s, 2H, CH=CH); 7.74 (t, J = 7.8, 2H, Ar-Dipp-H); 7.60 (d, J = 7.9, 4H, Ar-Dipp-H); 2.25 (dt, J = 13.6, 6.8, 4H, iPr); 1.25 (d, J = 6.8, 12H, iPr); 1.22 (d, J = 6.8, 12H, iPr).

^{13}C NMR(DMSO-d_6, 151 MHz, δ, ppm): 144.6 (Ar) 132.5 (Ar) 129.7 (Ar) 127.7 (C=C) 127.6 (C-Br) 125.2 (Ar) 28.9 (iPr) 23.8 (iPr) 22.8 (iPr)

[(SIPr)Br]Br

Yield: 0.471 g (88%), white powder.

^{1}H NMR(DMSO-d_6, 600 MHz, δ, ppm): 7.61 (t, J = 7.8, 2H, Ar-Dipp-H); 7.49 (d, J = 7.8, 4H, Ar-Dipp-H); 4.66 (s, 4H, CH_2-N); 2.98 (dt, J = 13.5, 6.7, 4H, iPr); 1.35 (d, J = 6.7, 12H, iPr); 1.25 (d, J = 6.8, 12H, iPr).

^{13}C NMR (DMSO-d_6, 151 MHz, δ, ppm): 153.8 (C-Br); 145.9 (Ar); 131.7 (Ar); 130.1 (Ar); 125.4 (Ar); 53.7 (CH_2-N); 28.5 (iPr); 24.4 (iPr); 23.9 (iPr).

[(6-Dipp)Br]Br

Yield: 0.510 g (98%), white powder.

^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 7.48 (t, J = 7.8, 2H, Ar-Dipp-H); 7.29 (d, J = 7.7, 4H, Ar-Dipp-H); 4.47 (br.s, 4H, CH_2-N); 2.93 (t, J = 6.1, 4H, iPr); 2.82 (br.s, 2H, CH_2); 1.40 (d, J = 6.0, 12H, iPr); 1.30 (d, J = 6.4, 12H, iPr).

^{13}C NMR ($CDCl_3$, 101 MHz, δ, ppm): 148.8 (C-Br); 144.5 (Ar); 139.1 (Ar) 131.4 (Ar) 125.7 (Ar); 54.1 (CH_2-N); 29.4 (iPr); 25.5 (iPr) 23.9 (CH_2).

[(7-Dipp)Br]Br

Yield: 0.493 g (93%), white powder.

^{1}H NMR(DMSO-d_6, 600 MHz, δ, ppm): 7.52 (t, J = 8.1, 2H, Ar-Dipp-H); 7.45 (d, J = 7.9, 4H, Ar-Dipp-H); 4.48 (br.s, 4H, CH_2-N); 2.95 (q, J = 6.8, 4H, iPr); 2.35 (br.s, CH_2CH_2); 1.36 (d, J = 6.7, 12H, iPr); 1.27 (d, J = 6.8, 12H, iPr).

^{13}C NMR (151 MHz, DMSO-d_6, δ, ppm): 154.9 (C-Br); 143.3 (Ar); 141.5 (Ar); 130.7 (Ar); 125.7 (Ar); 57.7 (N-CH2); 28.7 (iPr) 24.4 (iPr) 23.6 (iPr) 23.0 (CH_2CH_2).

4.5 General procedure for reaction of free carbenes with copper(II) salts.

Solution of carbene in ether (approx. 1 g in 30 ml) was added to the suspension of copper salt (1 eq) in small amount of ether. Mixture intensively stirred 24 h and then precipitate filtered off. In case of Cu(OAc)2 this method gave pure complexes. In case of $CuBr_2$ and $CuCl_2$ a mixtures of nonparamagnetic products was obtained. Mixture of [(6-Mes)$_2$Cu][$CuBr_2$] and [(6-Mes)Br][$CuBr_2$] was separated by means of fractional crystallization from THF.

IMesCu(OAc)$_2$

Yield: 0.931 g (88%) green powder.

Anal. Calcd for $C_{25}H_{30}CuN_2O_4$: C, 61.78; H, 6.22; N, 5.76. Found: C, 62.86; H, 6.05; N, 5.63

(5-Mes)Cu(OAc)$_2$

Yield: 0.864 g (81%) blue powder.

Anal. Calcd for $C_{25}H_{32}CuN_2O_4$: C, 61.52; H, 6.61; N, 5.74. Found: C, 60.67; H, 6.43; N, 5.81

(6-Mes)Cu(OAc)$_2$

Yield: 0.562 g (52%) blue powder.

Anal. Calcd for $C_{26}H_{34}CuN_2O_4$: C, 62.19; H, 6.83; N, 5.58. Found: C, 63.94; H, 6.69; N, 5.62

(7-Mes)Cu(OAc)$_2$

Yield: 0.448 g (49%) green powder.

Anal. Calcd for $C_{27}H_{36}CuN_2O_4$: C, 62.83; H, 7.03; N, 5.43. Found: C, 61.98; H, 7.15; N, 5.34

(5-Dipp)Cu(OAc)$_2$

Yield: 0.912 g (89%) green powder.

Anal. Calcd for $C_{31}H_{44}CuN_2O_4$: C, 65.07; H, 7.75; N, 4.90. Found: C, 66.20; H, 7.62; N, 4.97

[(6-Mes)$_2$Cu][CuBr$_2$]

Yield: 0.763 g (59% relative to free carbene) white powder.

^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 6.89 (s, 4H, Ar-Mes-H); 3.08 (br.s, 4H, CH_2-N); 2.34 (s, 6H, CH_3-Mes); 2.09 (br.s, 2H); 1.74 (s, 12H, CH_3-Mes).

^{13}C NMR ($CDCl_3$, 101 MHz, δ, ppm): 198.7 (N-C-N); 141.5 (Ar); 138.2 (Ar); 134.8 (Ar); 129.8 (Ar); 44.4 (N-CH_2); 21.2 (CH_3-Mes) 20.6 (CH_2) 18.0 (CH_3-Mes).

[(6-Mes)Br][Br]

Yield: 0.392 g (29%) white powder.

^{1}H NMR($CDCl_3$, 400 MHz, δ, ppm): 7.01 (s, 4H, Ar-Mes-H); 4.29 (br.s, 4H, CH_2-N); 2.81 (br.s, 2H, CH_2); 2.26-2.36 (m, 18H, CH_3-Mes).

^{13}C NMR ($CDCl_3$, 101 MHz, δ, ppm): 148.8 (C-Br); 140.9 (Ar); 139.2 (Ar); 133.5 (Ar); 130.5 (Ar); 51.8 (N-CH_2); 21.1 (Me-Ar); 20.4 (CH_2); 18.3 (Me-Ar).

4.6 Reaction of (5-Dipp)Cu(OAc)$_2$ with water.

Copper complex (30 mg) was dissolved in 0.6 ml of wet $CDCl_3$. After 20 min solution was turned color from deep blue to green. After 2 hours the solution became colorless, and some green precipitate was formed. ^{1}H, ^{13}C NMR of this solution was found to be identical with published spectra of (5-Dipp)*H_2O[4].

2. X-ray crystal structure determination.

Data were collected on a Bruker SMART APEX II CCD (compounds **[(6-Dipp)Br]$_2$[Cu$_2$Br$_6$]** and **[(6-Dipp)Br][CuBr$_2$]**) and a Bruker SMART 1K CCD (compound **(6-Dipp)Br$_2$**) diffractometers (λ(Mo$K\alpha$)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program (versions 2.03 (compounds **[(6-Dipp)Br]$_2$[Cu$_2$Br$_6$]** and **[(6-Dipp)Br][CuBr$_2$]**) [S1] and 2.01 (compound **(6-Dipp)Br$_2$**) [S2]). For details, see Tables S1-S5. The structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms in compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters (U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and U_{iso}(H) = 1.2U_{eq}(C) for the other groups). All calculations were carried out using the SHELXTL program [S3]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center. CCDC 794664, 794665, 794666, 794667, 794668 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

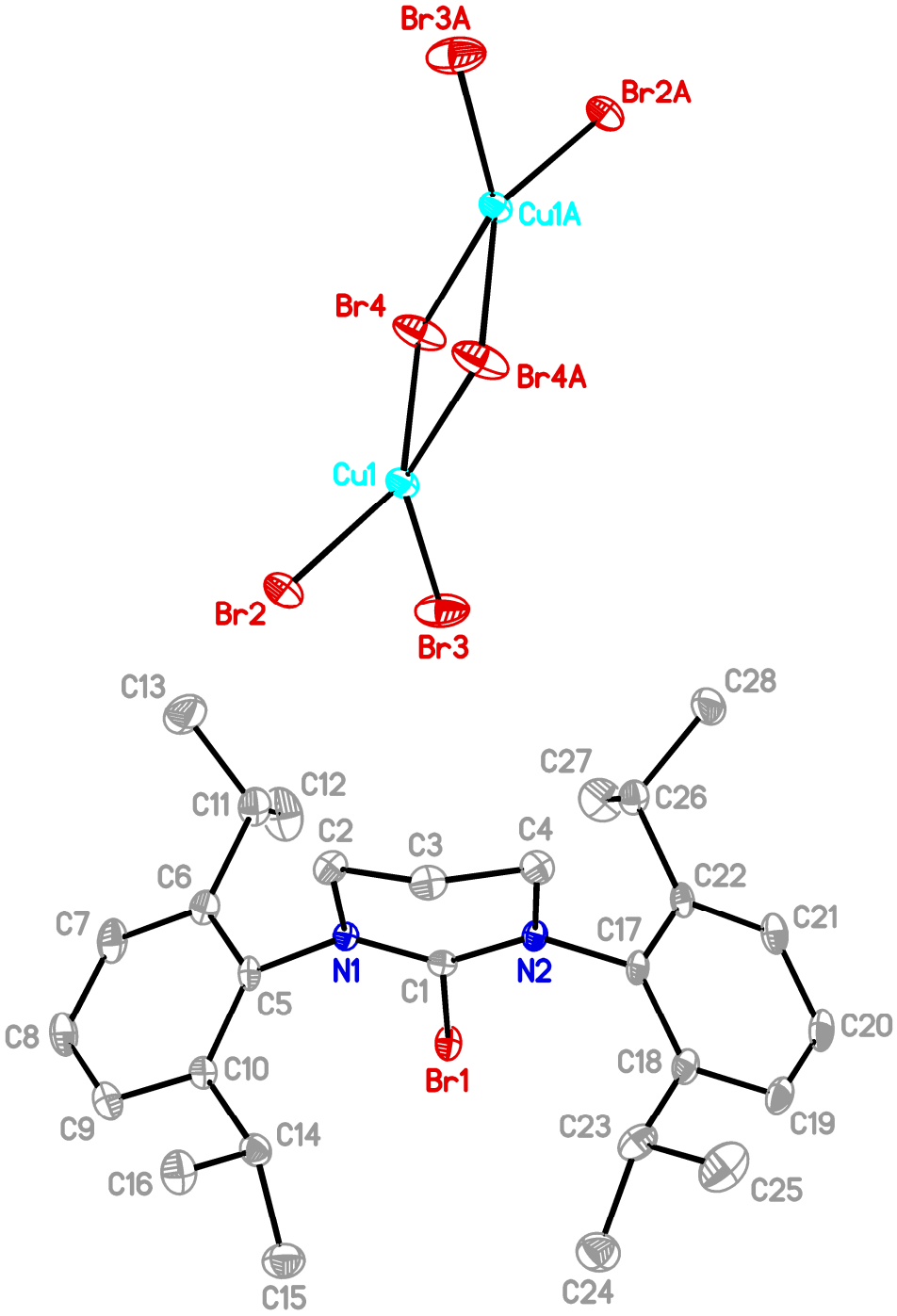

Fig. S1. Crystal structure of **[(6-Dipp)Br]$_2$[Cu$_2$Br$_6$]** with 40% probability ellipsoids (hydrogen atoms are omitted for clarity). The label A denotes symmetrically equivalent atom relative to the inversion center.

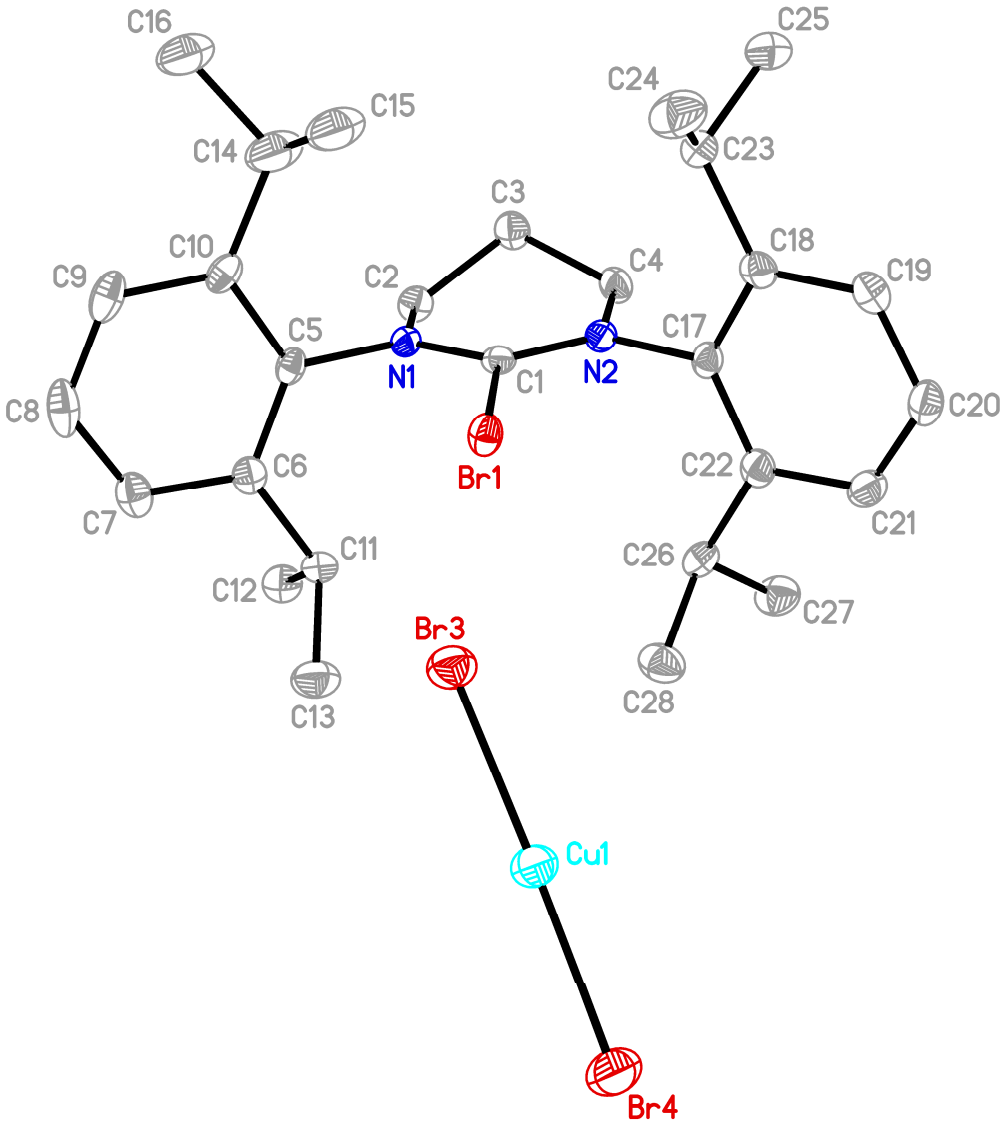

Fig. S2. Crystal structure of **[(6-Dipp)Br][CuBr$_2$]** with 40% probability ellipsoids (hydrogen atoms are omitted for clarity).

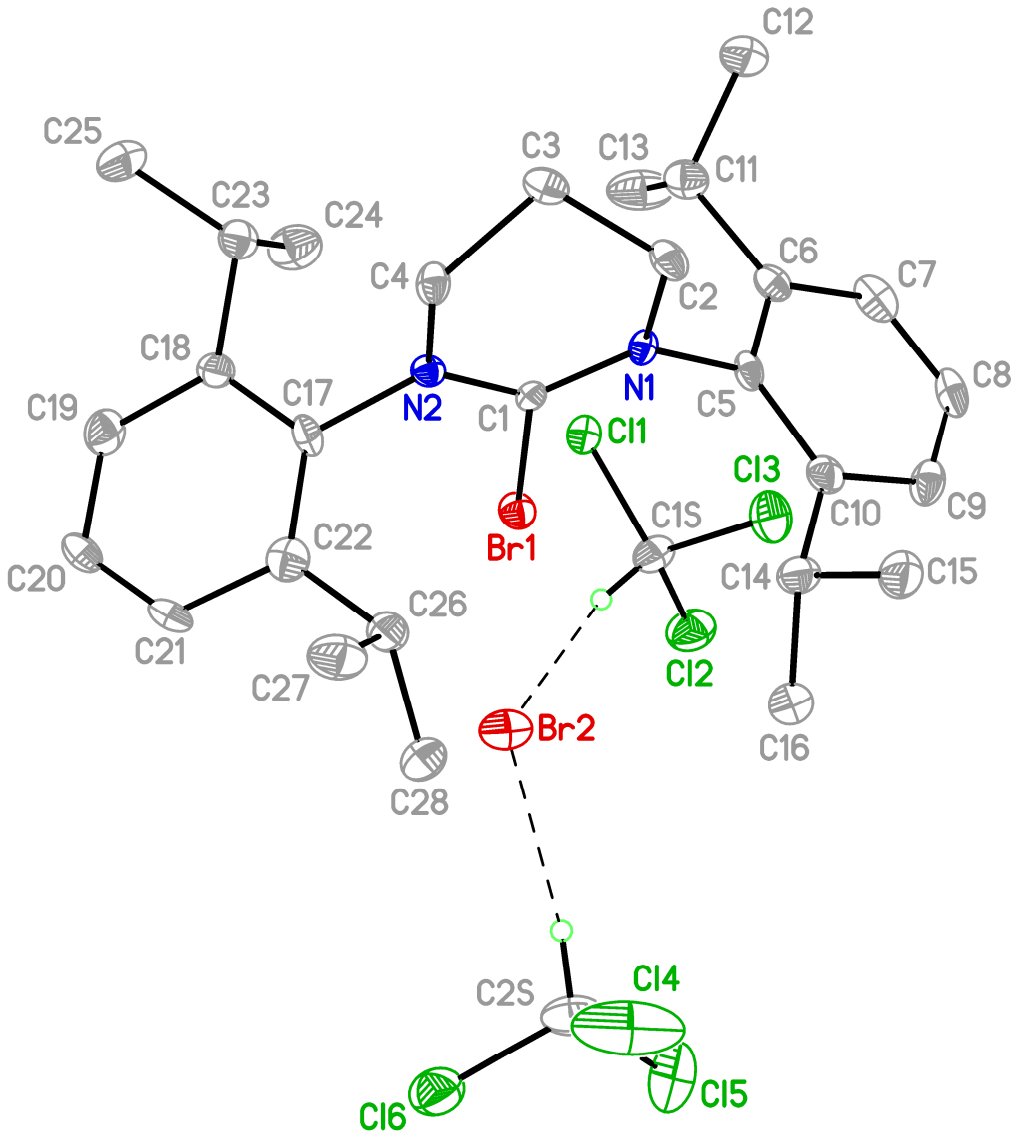

Fig. S3. Crystal structure of [(6-Dipp)Br][Br] with 40% probability ellipsoids (only hydrogen atoms of the solvate chloroform molecules are depicted). The intermolecular C-H…Br hydrogen bond interactions are shown by dashed lines.

Table S1. Crystal data and structure refinement for **[(6-Dipp)Br]$_2$[Cu$_2$Br$_6$]**.

Empirical formula	C28 H40 Br4 Cu N2	
Formula weight	787.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6908(10) Å	α = 91.270(2)°.
	b = 10.7644(10) Å	β = 102.251(2)°.
	c = 14.4174(14) Å	γ = 106.937(2)°.
Volume	1544.8(3) Å^3	
Z	2	
Density (calculated)	1.694 Mg/m^3	
Absorption coefficient	5.899 mm^{-1}	
F(000)	782	
Crystal size	0.30 x 0.20 x 0.18 mm^3	
Theta range for data collection	1.45 to 32.75°.	
Index ranges	-16<=h<=16, -16<=k<=16, -21<=l<=21	
Reflections collected	31556	
Independent reflections	11257 [R(int) = 0.0476]	
Completeness to theta = 32.75°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.347 and 0.201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11257 / 0 / 324	
Goodness-of-fit on F^2	1.007	
Final R indices [for 8589 rflns with I>2σ(I)]	R1 = 0.0368, wR2 = 0.0840	
R indices (all data)	R1 = 0.0588, wR2 = 0.0910	
Largest diff. peak and hole	1.642 and -1.437 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **[(6-Dipp)Br][$CuBr_2$]**.

Empirical formula	C28 H40 Br3 Cu N2	
Formula weight	707.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.4962(9) Å	α = 90°.
	b = 19.3988(9) Å	β = 91.8270(10)°.
	c = 15.5513(7) Å	γ = 90°.
Volume	5878.6(5) $Å^3$	
Z	8	
Density (calculated)	1.600 Mg/m^3	
Absorption coefficient	4.840 mm^{-1}	
F(000)	2848	
Crystal size	0.30 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.48 to 27.97°.	
Index ranges	-25<=h<=25, -25<=k<=25, -20<=l<=20	
Reflections collected	65975	
Independent reflections	14107 [R(int) = 0.0566]	
Completeness to theta = 27.97°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.444 and 0.325	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14107 / 0 / 605	
Goodness-of-fit on F^2	1.001	
Final R indices [for 10102 rflns with I>2σ(I)]	R1 = 0.0338, wR2 = 0.0631	
R indices (all data)	R1 = 0.0651, wR2 = 0.0717	
Largest diff. peak and hole	0.741 and -0.744 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **(6-Dipp)Br_2**.

Empirical formula	C30 H42 Br2 Cl6 N2	
Formula weight	803.16	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 10.9457(12) Å	α = 90°.
	b = 21.357(2) Å	β = 95.597(2)°.
	c = 15.7609(17) Å	γ = 90°.
Volume	3666.8(7) $Å^3$	
Z	4	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	2.67 mm^{-1}	
F(000)	1632	
Crystal size	0.24 x 0.20 x 0.06 mm^3	
Theta range for data collection	1.61 to 28.00°.	
Index ranges	-14<=h<=14, -28<=k<=28, -20<=l<=20	
Reflections collected	36710	
Independent reflections	8795 [R(int) = 0.0673]	
Completeness to theta = 28.00°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.852 and 0.532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8795 / 0 / 369	
Goodness-of-fit on F^2	0.871	
Final R indices [for 4225 rflns with I>2σ(I)]	R1 = 0.0574, wR2 = 0.1252	
R indices (all data)	R1 = 0.1278, wR2 = 0.1398	
Largest diff. peak and hole	0.900 and -0.883 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for **(IMes)Cu(OAc)$_2$**.

Empirical formula	C25 H30 Cu N2 O4	
Formula weight	486.05	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.480(3) Å	α = 83.440(7)°.
	b = 12.416(4) Å	β = 73.973(6)°.
	c = 12.623(4) Å	γ = 71.022(6)°.
Volume	1207.5(7) Å^3	
Z	2	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.937 mm^{-1}	
F(000)	510	
Crystal size	0.36 x 0.32 x 0.08 mm^3	
Theta range for data collection	1.68 to 28.00°.	
Index ranges	-11<=h<=11, -16<=k<=16, -16<=l<=16	
Reflections collected	13026	
Independent reflections	5740 [R(int) = 0.0566]	
Completeness to theta = 28.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.729	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5740 / 0 / 297	
Goodness-of-fit on F^2	1.007	
Final R indices [for 4417 rflns with I>2σ(I)]	R1 = 0.0810, wR2 = 0.2021	
R indices (all data)	R1 = 0.1008, wR2 = 0.2130	
Largest diff. peak and hole	1.716 and -1.148 e.Å^{-3}	

Table S5. Crystal data and structure refinement for **(6-Mes)Cu(OAc)$_2$**.

Empirical formula	C26 H34 Cu N2 O4	
Formula weight	502.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 23.7798(11) Å	α = 90°.
	b = 8.8383(4) Å	β = 134.8860(10)°.
	c = 16.8227(14) Å	γ = 90°.
Volume	2505.1(3) Å^3	
Z	4	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	0.905 mm^{-1}	
F(000)	1060	
Crystal size	0.20 x 0.20 x 0.02 mm^3	
Theta range for data collection	2.42 to 26.08°.	
Index ranges	-29<=h<=29, -10<=k<=10, -20<=l<=20	
Reflections collected	11686	
Independent reflections	4837 [R(int) = 0.0299]	
Completeness to theta = 26.08°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.982 and 0.840	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4837 / 101 / 156	
Goodness-of-fit on F^2	1.018	
Final R indices [for 4104 rflns with I>2σ(I)]	R1 = 0.0757, wR2 = 0.1762	
R indices (all data)	R1 = 0.0963, wR2 = 0.1994	
Absolute structure parameter	0.26(3)	
Largest diff. peak and hole	0.842 and -0.618 e.Å^{-3}	

3. References.

(1) Hintermann, L. *Beilstein Journal of Organic Chemistry* **2007**, *3*, No 22.

(2) Iglesias, M.; Beetstra, D. J.; Knight, J. C.; Ooi, L.-L.; Stasch, A.; Coles, S.; Male, L.; Hursthouse, M. B.; Cavell, K. J.; Dervisi, A.; Fallis, I. A. *Organometallics* **2008**, *27*, 3279.

(3) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *The Journal of organic chemistry* **1997**, *62*, 7512.

(4) (a) Emin Günay, M.; Özdemir, N.; Ulusoy, M.; Uçak, M.; Dinçer, M.; Çetinkaya, B. *Journal of Organometallic Chemistry* **2009**, *694*, 2179(b) Kantchev, E. A. B.; Ying, J. Y. *Organometallics* **2008**, *28*, 289.

(5) G.M.Sheldrick, *SADABS, v. 2.03*, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, **2003**.

(6) G.M.Sheldrick, *SADABS, v. 2.01*, Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS, Madison, Wisconsin, **1998**.

(7) G.M.Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122.