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Synthesis and structural chemistry of oxazolinyl-carbene copper(I) complexes

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Abstract

Reaction of a series of directly connected oxazoline–imidazolium salts with potassium *tert*-butoxide and in the presence of $CuBr \cdot SMe_2$ at −78 °C cleanly gave the corresponding 2-oxazolinyl-(*N*-mesityl)imidazolidenecopper(I) complexes which are monomeric in solution but aggregate in the solid state. X-ray diffraction studies established a dimeric structure for [{2-(4,4-dimethyl)-oxazolinyl-(*N*-mesityl)imidazolidene}(bromo)copper(I)]$_2$ (**2a**) whereas the chiral derivative [{2-(4-*S*-isopropyl)-oxazolinyl-(*N*-mesityl)imidazolidene}(bromo)-copper(I)]$_\infty$ (**2b**) forms infinite chains of a coordination polymer.

Keywords: *N*-heterocyclic carbene; Oxazoline; Copper; Coordination polymer

1. Introduction

The first copper(I) complex of an *N*-heterocyclic carbene ligand was reported by Arduengo et al. [1] more than a decade ago. Whereas this study was aimed at the exploration of ligating capabilities of this new class of ligands [2], their systematic application in copper chemistry has only recently begun.

Copper(I) complexes bearing *N*-heterocyclic carbene ligands have not only displayed interesting organometallic reactivity [3–6] and served as objects of study for carbene–metal bonding [7], but are beginning to be widely exploited in homogeneous catalysis [8–10]. This is to be seen in the general context of the research into the potential of NHC ligands as ancillary ligands in molecular catalysis, a field opened up by the work of Herrmann et al. [11]. *N*-heterocyclic carbenes have emerged as a family of ligands for homogeneous catalysis which act as σ-donors (as well as weak π-acceptors). In many respects these new ancillary ligands were found to resemble phosphorus donor ligands rather than classical Fischer or Schrock type carbenes. NHC ligands may therefore inter alia replace phosphine units in heterodonor ligands in combination with more "classical" ligand functionalities based on nitrogen or oxygen functionalities [12,13]. A combination with a considerable potential in stereoselective catalysis appears to be their combination with oxazolines in bidentate chelating ligand systems [14,15].

We recently developed a new family of chiral stereodirecting ligands based on a direct, single step coupling of a *N*-heterocyclic carbene unit with a chiral oxazolinyl moiety [16]. Such a modular approach provided inter alia the basis for an efficient search strategy for a new family of asymmetric rhodium hydrosilylation catalysts

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for prochiral dialkyl ketones. The ligands themselves are chelating the metal centres of the group 9 and 10 metals giving rise to small bite angles and relatively strained metal ligand structures. We were therefore interested to study their coordinating behaviour vis-à-vis metals which would not reinforce such a strained chelation, such as the monovalent group 11 metals. In this paper, we report the synthesis and characterization of various copper(I) complexes that contain both achiral and chiral oxazolinylcarbene ligands.

2. Results and discussion

For the synthesis of the copper complexes the oxazoline–imidazolium salts **1a–d** employed in this study were reacted with potassium *tert*-butoxide and in the presence of $CuBr \cdot SMe_2$ at −78 °C. This method has been previously reported by Sadighi and Buchwald [8c] and requires lower reaction temperatures than the deprotonation of the imidazolium salts with the basic Cu_2O [17]. Following this protocol, the desired copper complexes **2a–d** were isolated in 85–98% yield (Scheme 1) as pale white, air-sensitive powders after filtration of the KBr salt and washing of the crude product with pentane.

The formation of the carbene complexes was confirmed by ^{13}C NMR spectroscopy, the characteristic resonance of *N*-heterocyclic carbene carbon nuclei being observed at δ 179–182 ppm. In solution, the ^{1}H and ^{13}C NMR spectra of all four compounds are consistent with their maximum effective symmetry and thus mononuclear nature in solution. For achiral compound **2a** this implies that the two methyl groups of the oxazoline ring are chemically equivalent as are the two *meta*-protons of the mesityl ring. A small but significant coordination shift of the *C*(=N)O ^{13}C NMR resonance (152.5 ppm) in comparison with the ligand precursor (148.8 ppm) indicates at least weak coordination of the oxazoline ring to the metal centre. This notion is also supported by the slightly shifted oxazoline *v*(C=N) vibrational band which is observed at lower wavenumbers (1686 cm^{-1}) compared to the free oxazoline (1691 cm^{-1}). In the same way, the NMR spectra of complex **2b** display a significant coordination shift of the *C*(=N)O ^{13}C NMR resonance (153.8 ppm) in comparison with the ligand precursor (149.4 ppm) as well as the shifted oxazoline *v*(C=N) vibrational band (1674 cm^{-1}) compared to the free oxazoline at 1696 cm^{-1} are consistent with the structure represented in Scheme 1. The ^{1}H NMR spectrum of complex **2b**, displaying the characteristic signal pattern for this type of complex is displayed in Fig. 1.

A similar behaviour was observed for the other two complexes, **2c** and **2d**. In summary, while there is some indication of weak oxazoline coordination based on the chemical coordination shifts, which we observed, the role of the oxazoline binding *in solution* could not be unambiguously established. This is indicated in the structures proposed in Scheme 1.

Single crystals of **2a** were grown by slow diffusion of pentane into a solution of the complex in dichloromethane. The molecular structure is displayed in Fig. 2 along

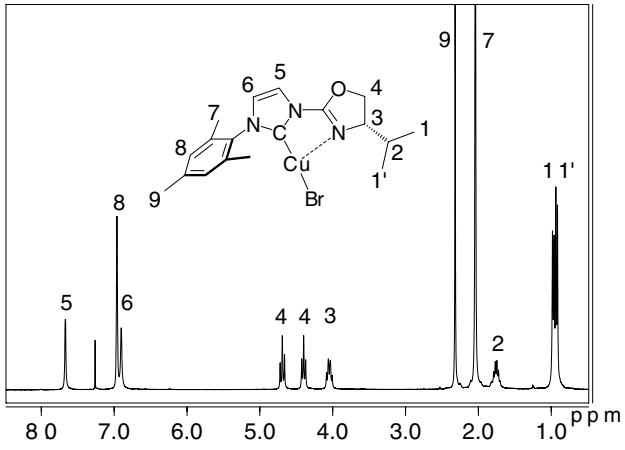
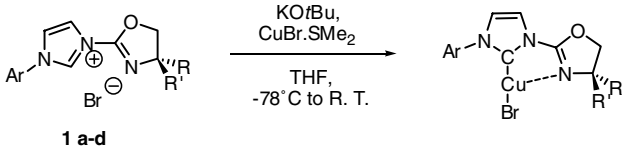


Fig. 1. ^{1}H NMR spectrum of complex **2b** recorded at 298 K in $CDCl_3$.



1	Ar	R'	R
1a	Mes	Me	Me
1b	Mes	H	iPr
1c	Mes	H	tBu
1d	Ph_2CH-	H	tBu

Scheme 1. Synthesis of the copper(I) complexes (**2a–d**) from imidazolium (**1a–d**).

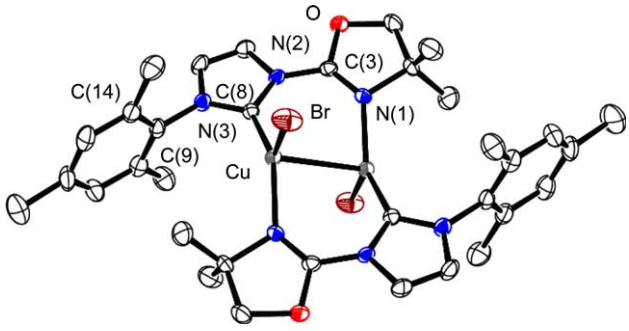


Fig. 2. Molecular structure of **2a**. Selected bond lengths (Å) and angles (°): Cu–Br, 2.4475(7); Cu–C(8), 1.905(4); Cu–N(1), 1.998(3); Cu–Cu, 2.707(1) and C(8)–Cu–Br, 116.9(1); N(1)–Cu–Br, 97.9(1); C(8)–Cu–N(1), 142.8(2); C(14)–C(9)–N(3)–C(8), 105.4(2); C(8)–N(2)–C(3)–N(1), 18.3(2).

with the principal bond lengths and angles. Complex **2a** crystallizes as a centrosymmetric dimer with the two oxazolinylcarbene ligands bridging the two copper centers. The geometry around the metal center may be viewed as a distorted trigonal pyramid with the bromine in the apical position. The Cu–C bond distance is within the range reported in the literature [1.905(4) Å] [3–10]. The mesityl ring is slightly twisted from this usual orthogonal position to the imidazolyl ring [dihedral angle: C(14)–C(9)–N(3)–C(8) 105.4°], probably due to a steric interaction with the bromine. We also note that the geometry around the copper enforces a slight twist of the heterocycles in the ligand. [C(8)–N(2)–C(3)–N(1) 18.3°]. The copper–copper distance of 2.707(1) Å is in the range observed previously for oligonuclear Cu^{I}-species and has been interpreted in terms of a weak metallophilic closed shell (d^{10}–d^{10}) interaction [18]. However, it should be pointed out, that the close proximity of the metal centres is a consequence of the bridging coordination of the oxazoline carbenes and that the intermetal distance may be a manifestation of a lack of antibonding rather than due to a significant attractive interaction.

Single crystals of the chiral complex **2b** suitable for an X-ray diffraction study were obtained from dichloromethane/pentane giving the coordination polymer shown in Fig. 3. The copper is in a trigonal environment with C(1), Cu, N(3), Br in the same plane (Fig. 3(a)). Each copper is connecting a carbene moiety of one ligand with the oxazoline ring of a second ligand and the *N*-bonded mesityl rings in the bidentate ligands are disposed almost orthogonally to the imidazolyl ring

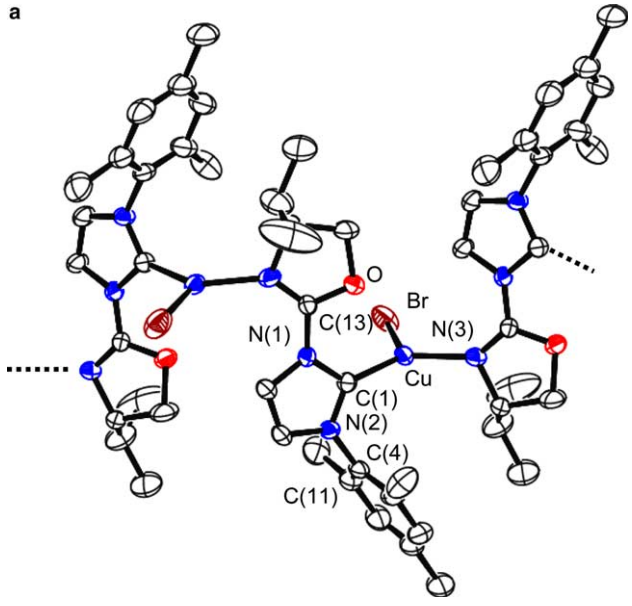


Fig. 3. (a) Molecular structure of **2b**. Selected bond lengths (Å) and angles (°): Cu–C(1), 1.891(4); Cu–N(3), 1.968(5); Cu–Br, 2.4306(7) and C(1)–Cu–N(3), 134.52(5); C(1)–Cu–Br, 112.4(1), N(3)–Cu–Br, 112.74(4); (b) View of the structure of the polymer **2b**.

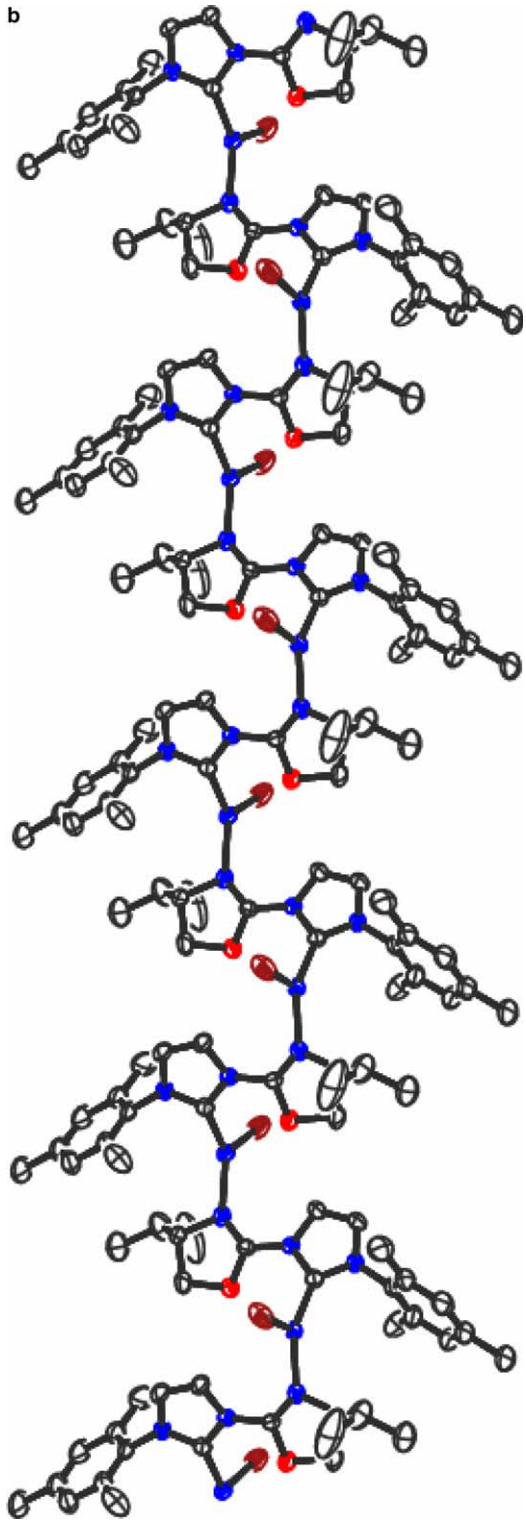


Fig 3. (*continued*)

[dihedral angle: C(11)–C(4)–N(2)–C(1) 85.3°]. The polymer chain is composed by an alternative arrangement of the ligands giving a linear conformation with a C_2-symmetric axis, the separation between two identical ligand units being 10.499 Å. The Cu–C bond distance was found to be 1.891(4) Å and thus similar to **2a**.

3. Conclusions

We have shown that oxazolinylcarbene copper(I) complexes can be readily prepared according to the method reported by Sadighi and Buchwald. The considerable intra-ligand strain previously observed in the group 9 and 10 metal complexes of these ligands weakens their capability of chelating metal centres as is indicated by the small coordination shifts found in the IR and NMR spectra of their monomeric Cu^{I}-complexes recorded in solution. This also appears to lead to the formation of coordination oligo- or polymers in the solid state structures of these copper compounds. This is exemplified by the dimeric structure of the complex **2a**, bearing the achiral 2-(4,4-dimethyl)-oxazolinyl imidazolidene ligand whereas a coordination polymer material was obtained using 2-(4-*S*-isopropyl)-oxazolinyl imidazolidene ligand system in **2b**. In order to stabilize the monomeric complexes, the relative arrangement of the oxazoline and the NHC-units will have to be changed, allowing for larger chelate bite angles.

4. Experimental

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified and dried by standard methods. Ligands **1a**–**d** were synthesized according to literature procedures [16a,16b,16c,16d]. All other reagents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz and were referenced using the residual proton solvent peak. Infrared spectra were obtained on a FT-IR Perkin Elmer 1600. FAB mass spectra were recorded at the Anorganisch-Chemisches Institut, Universität Heidelberg. Elemental analysis were performed by the ''service commun d'analyse élémentaire of the Strasbourg Chemistry Department''.

4.1. (1-(4,4-dimethyloxazolin-2-yl)-3-mesitylimidazol-2-ylidene)copper(I) bromide (**2a**)

A solution of the imidazolium salt **1a** (200 mg, 0.55 mmol) and $CuBr \cdot SMe_2$ (113 mg, 0.55 mmol) in THF (15 mL) was cooled to −78 °C. To this solution was slowly added a solution of KO*t*Bu (68 mg, 0.61 mmol) in THF (6 mL) and the resulting bright yellow mixture was allowed to react overnight. After centrifugation the supernatant solution was separated and evaporated to dryness. Purification by washing with pentane (2 × 10 mL) gave compound **2b**, which was isolated as a white powder (219 mg, 93%). Upon crystallization from CH_2Cl_2/pentane colorless crystals were obtained which were suitable for an X-Ray diffraction experiment.

^{1}H NMR ($CDCl_3$, 298 K): δ 7.75 (d, $^{3}J = 2.0$ Hz, 1H, CH_{im}), 6.98 (s, 2H, CH_{mes}), 6.92 (d, $^{3}J = 2.0$ Hz, 1H, CH_{im}), 4.42 (s, 2H, C$H_{2\ oxa}$), 2.34(s, 3H, C$H_{3\ para}$), 2.05 (s, 6H, C$H_{3\ ortho}$), 1,45 (s, 6H, C$H_{3\ oxa}$); ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): δ 181.8 (N_2C), 152.5 (N*C*O), 139.9, 134.9, 134.5(C_{mes}), 129.6 (*C*H$_{mes}$), 123.0 (*C*H$_{im}$), 119.4 (*C*H$_{im}$), 81.6 (*C*H$_{2\ oxa}$), 67.4 ($C_{4\ oxa}$), 28.2 (*C*H$_{3\ oxa}$), 21.1 (*C*H$_{3\ para}$), 18.0 (*C*H$_{3\ ortho}$); FT-IR (KBr): 1686.5 cm^{-1} (s, $\nu_{(C=N)}$); MS (FAB+) *m*/*z* (%) : 490.2 (100) $[LCu_2Br]^+$, 629.5 (95) $[L_2Cu]^+$, 773.4 (85) $[L_2Cu_2Br]^+$, 346.3 (65) $[LCu]^+$; Anal. Calc. for $C_{34}H_{42}Br_2Cu_2N_6O_2$ (853.64): C, 47.84; H, 4.96; N, 9.84. Found : C, 47.53; H, 5.09; N, 9.52%.

4.2. (1-((*S*)-4-iso propyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-ylidene) copper(I) bromide (**2b**)

Compound **2b** was synthesized from the imidazolium salt **1b** (200 mg, 0.52 mmol), $CuBr \cdot SMe_2$ (108 mg, 0.52 mmol) and KO*t*Bu (65 mg, 0.60 mmol) following the same procedure as for **2a**. It was isolated as an off-white powder (198 mg, 85%). Crystallisation from CH_2Cl_2/pentane gave colourless crystals suitable for an X-ray diffraction experiment.

^{1}H NMR ($CDCl_3$): δ 7.72 (d, $^{3}J = 2.0$ Hz, 1H, CH_{im}), 6.98 (s, 2H, CH_{mes}), 6.91 (d, $^{3}J = 2.0$ Hz, 1H, CH_{im}), 4.74 (dd, $^{2}J = 8.4$ Hz, $^{3}J = 9.4$ Hz, 1H, C$H_{2\ oxa}$), 4.43 (t, $J = 8.2$ Hz, 1H, C$H_{2\ oxa}$), 4.10 (m, 1H, CH_{oxa}), 2.33 (s, 3H, C$H_{3\ para}$), 2.05 (s, 3H, C$H_{3\ ortho}$), 1.85 (m, 1H, C*H*(CH$_3$)$_2$), 1.07 (d, $^{3}J = 6.7$ Hz, 3H, CH(CH_3)$_2$), 0.98 (d, $^{3}J = 6.8$ Hz, 3H, CH(CH_3)$_2$); ^{13}C {^{1}H} NMR ($CDCl_3$): δ 182.4 (N_2C), 153.8 (N*C*O), 139.8 (C_{mes}), 135.0 (C_{mes}), 134.5 (C_{mes}), 129.6 (*C*H$_{mes}$), 123.0 (*C*H$_{im}$), 72.9 (*C*H$_{2\ oxa}$), 71.2 (*C*H$_{oxa}$), 32.6 (*C*H(CH$_3$)$_2$), 21.1 (*C*H$_{3\ para}$), 19.0 (CH(*C*H$_3$)$_2$), 18.0 (CH(*C*H$_3$)$_2$), 17.8 (*C*H$_{3\ ortho}$); FT-IR (KBr): 1674 cm^{-1} (s, $\nu_{(C=N)}$); MS (FAB+) *m*/*z* (%) : 801.4 (100) $[L_2Cu_2Br]^+$, 504.2 (32) $[LCu_2Br]^+$, 657.6 (30) $[L_2Cu]^+$, 360.3 (25) $[LCu]^+$; Anal. Calc. for $C_{18}H_{23}BrCuN_3O$ (440.84): C, 49.04; H, 5.26; N, 9.53. Found : C, 46.50; H, 5.96; N, 8.79%.

4.3. (1-((*S*)-4-tert-butyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-ylidene) copper(I) bromide (**2c**)

Compound **2c** was synthesized from the imidazolium salt **1c** (200 mg, 0.51 mmol), $CuBr \cdot SMe_2$ (105 mg, 0.51 mmol) and KO*t*Bu (65 mg, 0.60 mmol) following the same procedure as for **2a**. It was isolated as an off-white powder (204 mg, 88%).

^{1}H NMR ($CDCl_3$): δ 7.71 (d, $^{3}J = 1.9$ Hz, 1H, CH_{im}), 6.97 (s, 1H, CH_{mes}), 6.97 (s, 1H, CH_{mes}), 6.92 (d, $^{3}J = 1.9$ Hz, 1H, CH_{im}), 4.67 (dd, $^{2}J = 8.2$ Hz, $^{3}J = 10.2$ Hz, 1H, C$H_{2\ oxa}$), 4.53 (t, $J = 8.4$ Hz, 1H, C$H_{2\ oxa}$), 4.13 (dd, $^{3}J = 8.2$ Hz, $^{3}J = 9.8$ Hz, 1H, CH_{oxa}), 2.33 (s, 3H, C$H_{3\ para}$), 2.05 (s, 3H, C$H_{3\ ortho}$), 2.04 (s, 3H, C$H_{3\ ortho}$), 1.01 (s, 9H, C(CH_3)$_3$); ^{13}C

{^{1}H} NMR ($CDCl_3$): δ 181.7 (N_2C), 153.6 (N*C*O), 139.8 (C_{mes}), 134.9 (C_{mes}), 134.3 (C_{mes}), 129.6 (CH_{mes}), 123.2 (CH_{im}), 119.2 (CH_{im}), 74.6 (CH_{oxa}), 71.9 ($CH_{2\ oxa}$), 33.9 ($C(CH_3)_3$), 25.8 (C(CH_3)$_3$), 21.1 ($CH_{3\ para}$), 17.9 ($CH_{3\ ortho}$), 17.9 ($CH_{3\ ortho}$); MS (FAB+) *m*/*z* (%) : 685.6 (100) $[L_2Cu]^+$, 374.3 (70) $[LCu]^+$, 312.4 (68) $[L+H]^+$, 829.4 (65) $[L_2Cu_2Br]^+$, 518.2 (45) $[LCu_2Br]^+$; FT-IR (KBr): 1685 cm^{-1} (s, $\nu_{(C=N)}$); Anal. Calc. for $C_{19}H_{25}BrCuN_3O$ (454.87): C, 50.17; H, 5.54; N, 9.24. Found : C, 48.66; H, 5.65; N, 9.09%.

4.4. (1-((*S*)-4-tert-butyl-4,5-dihydrooxazol-2-yl)-3-diphenylmethylmesitylimidazol-2-ylidene) copper(I) bromide (**2d**)

Compound **2d** was synthesized from imidazolium salt **1d** (200 mg, 0.45 mmol), $CuBr \cdot SMe_2$ (93 mg, 0.45 mmol) and KO*t*Bu (56 mg, 0.50 mmol) following the same procedure as for **2a**. It was isolated as an off-white powder (223 mg, 98%).

^{1}H NMR ($CDCl_3$): δ 7.51 (d, $^3J = 1.9$ Hz, 1H, CH_{im}), 7.40–7.31 (m, 6H, CH_{Ph}), 7.20–7.15 (m, 5H, $CH_{Ph} + CHPh_2$), 6.91 (d, $^3J = 1.9$ Hz, 1H, CH_{im}), 4.62 (dd, $^2J = 9.3$ Hz, $^3J = 9.3$ Hz, 1H, $CH_{2\ oxa}$), 4.48 (dd, $^2J = 8.5$ Hz, $^3J = 8.5$ Hz, 1H, $CH_{2\ oxa}$), 4.09 (dd, $^3J = 8.4$ Hz, $^3J = 9.6$ Hz, 1H, CH_{oxa}), 0.97 (s, 9H, C(CH_3)$_3$);^{13}C {^{1}H} NMR ($CDCl_3$): δ 179.1 (N_2C), 153.5 (N*C*O), 137.8, 137.8 (C_{Ph}), 129.1, 128.8, 128.7, 128.3, 128.2 (CH_{Ph}), 120.5 (CH_{im}), 119.1 (CH_{im}), 74.5 (CH_{oxa}), 71.9 ($CH_{2\ oxa}$), 69.6 ($CHPh_2$), 33.9 ($C(CH_3)_3$), 25.7 (C(CH_3)$_3$); MS (FAB+) *m*/*z* (%) : 442.3 (90) $[LCu]^+$, 781.6 $[L_2Cu]^+$, 925.4 (45) $[L_2Cu_2Br]^+$, 566.2 (42) $[LCu_2Br]^+$; FT-IR (KBr): 1688 cm^{-1} (s, $\nu_{(C=N)}$); Anal. Calc. for $C_{23}H_{25}BrCuN_3O$ (502.91): C, 54.93; H, 5.01; N, 8.36. Found : C, 54.02; H, 5.19; N, 7.84%.

5. X-ray diffraction study of 2a and 2b

The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OPENMOLEN package was used [19]. The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors ($B(H) = 1.3B_{eqv}(C)$ Å^2) but not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were take from reference [20]. Crystal data and experimental details for the crystals of **2a** and **2b** are given in Table 1.

Table 1
X-ray experimental data of compounds **2a** and **2b**

	2a	**2b**
Formula	$C_{17}H_{21}BrCuN_3O$	$C_{18}H_{23}BrCuN_3O$
Molecular weight	426.83	440.85
Crystal system	Monoclinic	Monoclinic
Space group	$P12_1/c1$	$C121$
a (Å)	11.9618(2)	14.1818(3)
b (Å)	11.4097(3)	10.4988(3)
c (Å)	13.5678(3)	14.8370(4)
β (°)	91.046(5)	116.571(5)
V (Å^3)	1851.43(7)	1975.78(12)
Z	4	4
ρ_{calc} (g cm^{-3})	1.53	1.48
$F(000)$	864	896
μ (mm^{-1})	3.344	3.137
Temperature (K)	173	173
Wavelength (Å)	0.71073	0.71073
Radiation	Mo Kα graphite monochromated	
Number of data measured	9765	4179
Number of data with $I > 3\sigma(I)$	2890	3467
Number of variables	208	216
R	0.036	0.038
Rw	0.064	0.053
GOF	1.132	1.001

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 272539 and 272540. Copies of the data can be obtained free of charge on application to The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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