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Selective Copper-Mediated Halogenation of Aromatic Rings Under Mild Conditions

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A mild copper-mediated halogenation reaction of phenolic rings is reported. The reaction of bis(2-hydroxybenzyl)-1,3-diaminopropane (H_2bhbd) with copper(II) chloride in acetonitrile generates linear trinuclear $[Cu_3(bhcbd)_2Cl_2](CH_3CN)$, containing modified ligands, whose phenol moieties are selectively chlorinated at the 5-position. Under comparable experimental conditions with copper(II) bromide, bromination of the ligand is observed, albeit at a slower reaction rate. In the presence of trialkylorthoformates, which are used as dehydrating agents, a ring closure of the ligand is observed after removal of copper to yield a product with a six-membered ring. This product has been isolated and characterized by NMR spectroscopy and MS. Similarly, bromination of bis(2-hydroxybenzyl)-1,3-diiminopropane (H_2bhbdi) occurs in the presence of copper(II) bromide, with concomitant formation of a linear trinuclear complex. Surprisingly, an asymmetric dinuclear copper(II) coordination compound without chlorination of the ligand is obtained when the related ligand bis(2-hydroxybenzyl)-1,3-diminopropane (H_2bhbdi) reacts with copper(II) chloride.

Introduction

The halogenation of aromatic rings under mild conditions is hard to perform and the synthetic methods currently available are poorly selective.[1] Nature has developed a variety of elegant processes for halogenating specific substrates with regio- and stereoselectivity. Hence, an improved understanding of the biological routes to the halogenation of substrates could lead to the development of new efficient procedures. The discovery and characterization of naturally occurring enzymatic halogenation mechanisms has become an active area of research, increasing the number of known halogenating enzymes.[2,3]

Halogenases are divided into five different classes[4] whose structural characterization has provided a better mechanistic understanding of their (bio)chemical functioning. In fact, enzymatic systems are used nowadays to perform such selective reactions. For example, FAD-dependent halogenases[5] have been recently characterized and employed to achieve selective chlorination of aromatic rings, and nonheme halogenases have been used to chlorinate saturated hydrocarbons.[6] The use of enzymes to perform halogenation of small molecules is, however, expensive due to the purification procedure needed to recover the biocatalyst.

Coordination chemistry may help to improve the efficacy of such biomimetic processes to generate carbon–halogen bonds, as demonstrated by recent reports on the halogenation of alkanes and arenes[7–9] and on the halofunctionalization of olefins.[10] Carbon–halogen bond formation by reductive elimination has been extensively studied for many late transition metal centres, such as Pd,[11,12] Pt[13] and Rh,[14] and has been reported for Ni as well.[15,16] In contrast, Cu-mediated C–X (X = halogen) bond formation has received little attention, despite the obvious advantages of substituting expensive and/or toxic metals with a more environmentally friendly alternative in catalytic processes.

This study reports unique aerobic arene halogenations that have been carried out at room temperature using $CuCl_2$ or $CuBr_2$ as the source of chlorine or bromine and with dioxygen as the sole oxidant. The presence of the common dehydrating agent triethylorthoformate appears to be crucial to avoid side-reactions, i.e. hydroxylation, instead of halogenation.

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The structural formulae of the starting and modified ligands are depicted in Figure 1.

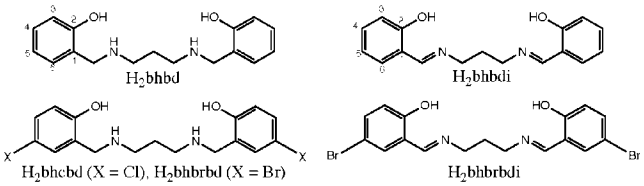

Figure 1. Structures of the starting ligand bis(2-hydroxybenzyl)-1,3-diaminopropane (H_2bhbd) and the final chlorinated or brominated ligand (H_2bhcbd or H_2bhbrbd, respectively); and bis(2-hydroxybenzyl)-1,3-diminopropane (H_2bhbdi) and the resulting brominated ligand (H_2bhbrbdi), with the ring numbering used.

The chlorination of a pyrazole ligand in the presence of copper(II) ions has been reported and the corresponding dinuclear copper(II) complex of the modified ligand was characterized by X-ray diffraction.[17] Previous studies of copper(II) coordination compounds from the ligand H_2bhbd have revealed the generation of linear trinuclear metal clusters.[18] These complexes were synthesized in methanol, and their characterization did not show any modification of the ligand structure.

Subsequent studies using the ligand H_2bhbdp [H_2bhbdp = 1,7-bis(2-hydroxyphenyl)-2,6-diaza-4-hydroxyheptane] with copper(II) chloride in acetonitrile yielded a trinuclear compound and a tetranuclear copper(II) cluster that also have been structurally characterized.[19] In this case, partial chlorination and hydroxylation of the ligand aryl groups at the 5-position have been observed. In contrast, the trinuclear copper(II) clusters prepared from H_2bhbdp and $CuCl_2$ in methanol were found not to exhibit such halogenation of the aromatic rings.[20]

As the solvent (acetonitrile) appears to be crucial for ligand modification, coordination reactions between CuX_2 and H_2bhbd in acetonitrile have now been carried out. In this study, it is shown that the selective and complete chlorination or bromination of the aromatic rings of the H_2bhbd ligand occurs in acetonitrile at room temperature, simply through reaction of the ligand with $CuCl_2$ or $CuBr_2$ in air and both in the presence or absence of a dehydrating agent, i.e. trimethyl- or triethylorthoformate.

When triethylorthoformate (eof) or trimethylorthoformate (mof) is present in the reaction mixture (used to avoid hydroxylation due to water traces), the main isolated product after copper removal, is a six-membered ring, apparently obtained by a condensation reaction involving the ligand and the alkylorthoformate.

The synthesis of copper(II) complexes with the related ligand H_2bhbdi [bis(2-hydroxybenzyl)-1,3-diiminopropane] has also been studied. Bromination of H_2bhbdi occurs in the presence of copper(II) bromide in acetonitrile, through the formation of a linear trinuclear copper(II) complex. UV/Vis studies allow clarification of the mechanistic features of the reaction.

Surprisingly, the reaction of H_2bhbdi with $CuCl_2$ in acetonitrile yields a dinuclear copper(II) complex which does not exhibit ligand modification, even in the presence of alkylorthoformate. In fact, with this ligand, the same coordination compounds are obtained in methanol and acetonitrile, as illustrated by single-crystal X-ray diffraction studies.

Results and Discussion

General

The reactions reported have been carried out in air, as dioxygen is required for the reaction to proceed; hence, no chlorination is observed under anaerobic conditions. The following Equation (1) describes the overall process, in the case of chlorination of H_2bhbd [H_4LH_2 in Equation (1)]:

$$3\ CuCl_2 + 3\ O_2 + 2\ H_4LH_2 \rightarrow Cu_3(LCl_2)_2Cl_2 + 6\ H_2O \quad (1)$$

Note that the H atoms listed in front of L denote acidic ionisable hydrogen atoms, whereas those listed behind L indicate aromatic H atoms that may be replaced by chloride ions.

The 5-position on the aromatic ring is most prominently activated through copper-mediated oxidation of the ligand; no reaction is found when Cu^{2+} is absent.

Bromination of H_2bhbd occurs under comparable reaction conditions with copper(II) bromide, but the process takes place at a slower rate. Contrary to the case of the chlorination, after 24 h, the reaction is not complete and the original ligand is still observed, together with mono- and dibrominated products, as detected by MS. The formation of polybrominated products clearly occurs before full conversion of the starting ligand.

A dinuclear copper(II) species [Cu_2(bhbdi)Cl_2] is obtained from methanol or acetonitrile reaction mixtures containing H_2bhbdi and copper(II) chloride. No modification of H_2bhbdi is observed in acetonitrile, under the reaction conditions used with H_2bhbd [H_2L2H_2 in Equations (2) and (3)].

The following Equation (2) describes the syntheses of such dinuclear copper(II) complexes:

$$2\ CuCl_2 + H_2L2H_2 \rightarrow Cu_2(L2H_2)Cl_2 + 2\ HCl \quad (2)$$

The reaction in presence of copper(II) bromide [Equation (3)] in acetonitrile leads to the formation of a trinuclear copper(II) cluster, and shows (partial) bromination of the 5-positions of the ligand aromatic rings, as deduced from X-ray diffraction and elemental analysis.

$$3\ CuBr_2 + 2\ O_2 + 2\ H_2L2H_2 \rightarrow Cu_3(L2Br_2)_2Br_2 + 4\ H_2O \quad (3)$$

Description of the structures of $[Cu_3(bhcbd)_2Cl_2](CH_3CN)$ (1), $[Cu_2(bhbdi)Cl_2]$ (2) and $[Cu_3(bhbrbdi)_2Br_2]$ (3)

The single-crystal X-ray analysis of **1**, depicted in Figure 2, shows that **1** is a trinuclear centrosymmetric complex,

consisting of three Cu^{2+} atoms in a linear arrangement, comparable to copper(II) clusters previously obtained from the same ligand in methanol.[18] The terminal metal centres, Cu(1) and Cu(1a) are in a hardly distorted square-pyramidal geometry. More geometric details are given in Table 1, and the crystallographic data are given in Table 2. The square base of the pyramid is formed by the N_2O_2 donor set from a $(bcbd)^{2-}$ ligand. At the apical position, a weakly coordinated Cl^- disordered over two positions is present (ratio 30:70). Details are given in Figure S1 and Table S1. The phenolate group acts as a bridging ligand, connecting the terminal copper to the central Cu(2) ion. The central copper atom Cu(2) is tetracoordinate in a square-planar environment with torsion angles O(1A)–Cu(2)–O(21)–Cu(1) of 159.3(2)° and O(21)–Cu(2)–O(1)–Cu(1) of 21.3(2)°, and Cl^- has a very weak interaction with Cu(2); see Figure S1. The Cu1–Cu2 distance is 2.9644(12) Å. The coordination environment of Cu(2) is formed by four phenolato O atoms from two bridging $bhbd^{2-}$ ligands. A packing diagram is given in Figure S2.

The molecular structure of **2** is shown in Figure 3. Compound **2** consists of a dinuclear asymmetric copper(II) unit, whose metal centres are tetracoordinated. The Cu(1) centre has a N_2O_2 square-planar coordination environment, whereas Cu(2) exhibits a distorted tetrahedral Cl_2O_2 geometry. The structure is characterized by torsion angles O(21)–Cu(2)–O(1)–Cu(1) of 9.14(7)° and N(9)–Cu(1)–O(1)–Cu(2) of 165.32(7)°. Details and packing are depicted in Figure 3, S3 and S4 and listed in Tables 1, 2 and S2.

The plane including the copper ions and the chloride ligands and the plane containing the copper centres and the ligand oxygen donors form a dihedral angle of 67.71°, and the distance between the copper(II) atoms is 3.0884(8) Å. The solid-state EPR spectrum, recorded at room temperature, is silent, indicative of a strong interaction between the two metal centres.

Table 1. Selected bond lengths [Å] and (dihedral) angles [°] for **1**, **2** and **3**.

1		**2**		**3**	
Cu1–O1	1.948(7)	Cu1–O1	1.951(1)	Cu1–O1	1.995(2)
Cu1–N9	2.007(7)	Cu1–N9	1.954(1)	Cu1–N9	1.970(3)
Cu1–Cl1B	2.570(12)	Cu1–Cu2	3.0884(8)	Cu1–Br1A	2.7181(6)
Cu1–Cl1A	2.540(3)	Cu1–O1	1.9710(17)	Cu1–Br1B	2.7480(12)
Cu1–N13	2.018(8)	Cu1–N13	1.9336(14)	Cu1–N13	1.949(3)
Cu1–O21	1.987(5)	Cu1–O21	2.0181(13)	Cu1–O21	1.968(2)
Cu2–O1	1.916(5)	Cu2–O1	1.9553(14)	Cu2–O1	1.956(2)
Cu2–O21	1.921(6)	Cu2–O21	2.1980(7)	Cu2–O21	1.942(2)
Cu1–Cu2	2.964(1)	Cu2–Cl1	2.2045(6)	Cu1–Cu2	2.8648(4)
Cu2–Cl1B	3.325(5)	Cu2–Cl2	99.33(7)	N13–Cu1–N9	97.44(11)
N9–Cu1–N13	94.9(3)	N9–Cu1–N13	76.62(6)	N9–Cu1–Br1A	112.32(8)
N9–Cu1–Cl1B	100.6(4)	O21–Cu1–O1	93.47(6)	N9–Cu1–Br1B	103.6(3)
O1–Cu1–N9	93.0(3)	O1–Cu1–N9	126.58(4)	O1–Cu1–N9	92.24(10)
O1–Cu1–O21	75.6(2)	O1–Cu2–Cl1	135.41(5)	O1–Cu1–O21	77.79(9)
O1–Cu2–O21	77.9(3)	O21–Cu2–Cl2	102.16(6)	O21–Cu2–O1	78.41(9)
Cu2–O1–Cu1	100.2(3)	Cu1–O1–Cu2	165.32(7)	Cu1–O1–Cu2	94.20(9)
N9–Cu1–O21	163.8(2)	N9–Cu1–O21	168.2(1)	N13–Cu1–O1	168.5(1)
N13–Cu2–O1	164.9(2)	N13–Cu1–O1	166.7(5)	N9–Cu2–O21	154.4(1)

Table 2. Crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{38}H_{38}Cl_4Cu_3N_6O_4$	$C_{17}H_{16}Cl_2Cu_2N_2O_2$	$C_{34}H_{21.9}Br_{2.10}Cu_3N_4O_4$
Molecular weight	975.16	478.30	918.96
Crystals system	monoclinic	monoclinic	monoclinic
T [K]	173(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Cell length [Å] (a, b, c)	13.767(2), 14.789(3), 10.758(2)	11.270(2), 8.391(2), 18.291(4)	8.9610(10), 10.7000(10), 17.321(2)
Cell angle [°] (β) (a, γ = 90°)	101.08(3)	97.64(3)	100.880(10)
Cell volume [Å^3]	2149.5	1714.4	1630.9
Z	2	4	4
$D_{calcd.}$ [mg/m^3]	1.507	1.853	1.871
F(000)	990	960	913
M [mm^{-1}]	1.764	2.806	4.557
Crystals size [mm]	0.20 × 0.20 × 0.05	0.30 × 0.27 × 0.10	0.10 × 0.10 × 0.10
θ_{min}, θ_{max} [°]	2.75–25.05	2.70–27.48	3.00–27.50
Reflections collected	35418	26155	28581
Independent reflections	3788 [R(int) = 0.0688]	3898 [R(int) = 0.0393]	3691 [R(int) = 0.0497]
R_1[a], wR_2[b], S[c]	0.0694, 0.1494, 1.309	0.0228, 0.0630, 1.104	0.0292, 0.0749, 1.174
Min/max residual density [e Å^{-3}]	–0.636, 0.732	0.4865, 0.7667	–0.472, 0.593

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. [c] Goodness-of-fit S = $[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

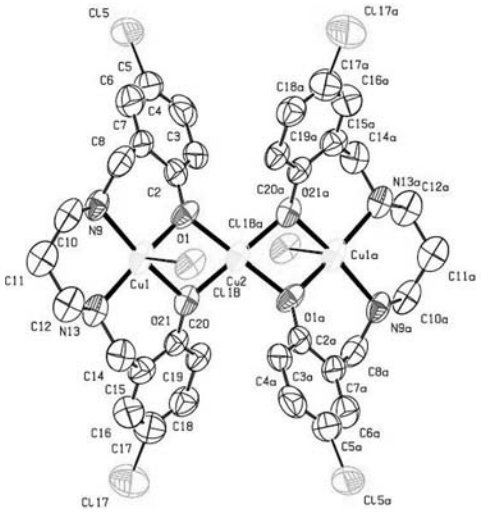

Figure 2. ORTEP representation of the molecular structure of the centrosymmetric trinuclear compound $[Cu_3(bhcbd)_2Cl_2](CH_3CN)$ (**1**), as determined by X-ray diffraction (only one of the disordered coordinated Cl ions is shown).

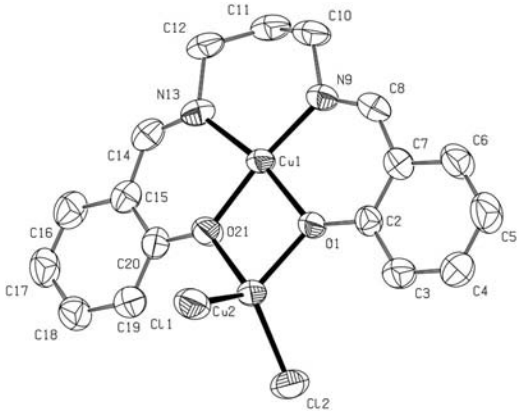

Figure 3. ORTEP representation of the molecular structure of the dinuclear compound $[Cu_2(bhbdi)Cl_2]$ (**2**), as determined by X-ray diffraction. The compound was isolated from a 1:1 (or a 1:2) mixture of the ligand H_2bhbdi and copper(II) chloride in acetonitrile, with or without the use of a dehydrating agent.

Partial bromination of H_2bhbdi is observed when copper bromide reacts with the ligand in acetonitrile (with a L/M ratio of 1:3). Single crystals of **3** have been obtained from several reaction mixtures, and X-ray diffraction studies revealed the partial bromination of the ligand 5-positions of the trinuclear linear copper(II) cluster obtained (see Figure 4 and S5). Packing details are given in Figure S6, and geometric details are given in Tables 1, 2 and S3. The geometry for Cu^I is distorted five-coordinate, as often seen for Cu^{II};[21] in fact $\tau = 0.17$, where τ is 0 and 1 for ideal square-pyramidal and trigonal-bipyramidal geometries, respectively.[22]

The 100% bromination of the 5-position would be given by the molecular formula $C_{34}H_{24}Br_6Cu_3N_4O_4$ (six Br atoms: two coordinated anions and four in the aromatic 5-positions). The 2–3% Br population at the 5-position found by XRD analysis is characterized by the formula

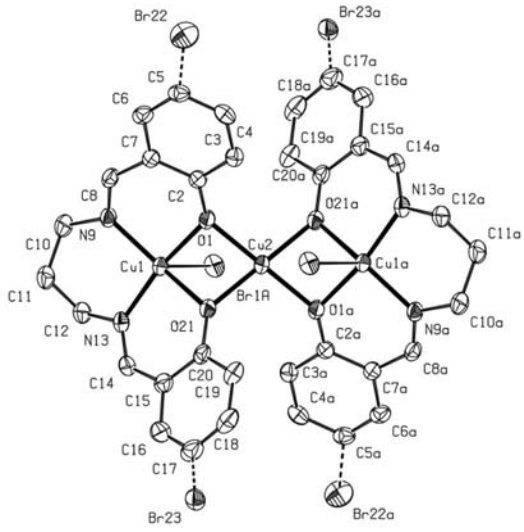

Figure 4. ORTEP representation of the molecular structure of the trinuclear compound $[Cu_3(bhbrbdi)_2Br_2]$ (**3**), as determined by X-ray diffraction. The ring bromination was estimated to be around 2–3%. H atoms were omitted for clarity, except at C5/17. Coordinated Br1 is disordered.

$C_{34}H_{21.9}Br_{2.10}Cu_3N_4O_4$ as specified in Table 2. Actually, the elemental analysis of the crystalline material (see Exp. Sect.) confirms that about 2.5% bromination of the ligand was achieved. As in **1**, the coordinated bromide is disordered over two positions (ratio 96:4) and also bridges the central Cu^{II} ion with Br–Cu = 3.06–3.17 Å.

Two more single crystal structures of reaction products were obtained with compositions close to that of **3**, i.e. **3a** and **3b**, and they are represented in Figures S7–S10, with geometric details given in Tables S4 and S5. Compounds **3** and **3a** differ slightly in the degree of ring bromination, but are basically the same and are 3–5% brominated in the ring. In **3b** the degree of monobromination observed is higher and corresponds to 35%; in this case acetonitrile is present as a sixth ligand, semicoordinated at 3.05 Å, with an unusually small Cu–N–C angle of 109°.

The coordination environment of Cu2 in all three cases is formed by four phenolato O atoms in the equatorial plane. The bromides axially coordinated to Cu1 are semicoordinated to the central Cu2 ion (Cu2–Br = on average 3.06 Å).

The Cu–Cu separation distances, Cu1–O1–O21–Cu2 torsions angles and τ parameters for **1**, **2** and **3** are presented in Table 3. Corresponding values for closely related alkoxido-bridged copper(II) complexes are included for comparison.

The τ values for **1** and **3** (listed in Table 3) are indicative of a slight distortion from square-pyramidal geometry in case of **3**. Other structural data for **1**, **2** and **3** were compared with those of other trinuclear linear alkoxido-bridged clusters with the same type of ligand, reported in our earlier work (Table 3).[20–22] It is seen that the Cu1–O1–O21–Cu2 torsion angle in the case of **3** is significantly smaller than that observed for the other compounds and for the related copper clusters obtained from bhbdp (**6**, **7** and **8**). This smaller torsion angle might be related to the size of the

Table 3. Selected bond lengths [Å] and (dihedral) angles [°] for a series of related alkoxido-bridged copper(II) compounds.

Complex	Cu–Cu	Cu1–O1–Cu2	O1–Cu2–O21	Cu1–O1–O21–Cu2	$\tau_{(Cu1)}$[b]	Ref.
$[Cu_3(bhcbd)_2Cl_2](CH_3CN)$ (**1**)	2.9644(12)	100.2(1)	77.9(3)	153.4(3)	0.02	[d]
$[Cu_2(bhbdi)Cl_2$ (**2**)][a]	3.0884(8)	102.2(1)	74.6(1)	168.55(1)	–	[d]
$[Cu_3(bhbrbdi)_2Br_2]$ (**3**)	2.8648(4)	94.2(1)	78.4(1)	141.2 (1)	0.23	[d]
$[Cu_3(bhbd)_2(CH_3OH)_2(ClO_4)_2]$ (**4**)	2.9852(7)	100.9(2)	79.1(1)	166.8(2)	0.03	[20]
$[Cu_3(bhbd)_2Cl_2](CH_3OH)_4$ (**5**)	2.9374(7)	98.4(1)	76.4(1)	154.58(18)	0.03	[20]
$[Cu_4(bhcbdp)_2(\mu\text{-}Cl)_2Cl_2](CH_3CN)$(**6**[c])	3.0855(9)	103.3(1)	78.6(1)	179.6(2)	0.22	[21]
$[Cu_3(bhbdp)_2(CH_3OH)_2(ClO_4)_2]$ (**7**)	2.9869(5)	101.1(1)	78.8(1)	165.18(15)	0.05	[22]
$[Cu_3(bhbdp)_2Cl_2(CH_3CN)_2](CH_3CN)_2$ (**8**)	2.9722(6)	97.5(1)	81.3(1)	156.30(10)	0.02	[21]

[a] Dinuclear copper(II) compound. [b] The τ parameter is used to characterize the geometry of five-coordinate compounds, between the trigonal bipyramid and the square-based pyramid. τ is calculated as $(\beta\text{-}\alpha)/60$, where α and β are opposite angles in the xy plane. The τ value ranges from 0 to 1. A value of zero characterizes a compound with a perfect square-pyramidal geometry, and a value of one symbolizes a perfect trigonal-bipyramidal geometry.[22] [c] Tetranuclear copper(II) compound. [d] This work.

axially coordinated bromide ion and may reflect a higher tension in the alkoxido bridge.

Characterization of the Modified Ligand After Copper(II) Removal

The chlorination of H_2bhbd has been studied for different metal/ligand ratios and as a function of time. For a proper characterization of the reaction mixture, the copper(II) is removed at the end of the reaction by addition of excess (4 equiv.) Na_2S, which produces a precipitate of copper sulfide. The copper-free products were analyzed by ^{1}H NMR and ESI-MS spectroscopy to detect any ligand modification. A detailed procedure is presented in the Supporting Information.

With a copper(II) chloride/H_2bhbd ratio of 3:1, after 24 h of reaction in air at room temperature in the presence of eof, complete conversion of the original ligand into mono- and dichlorinated species is observed (see below and the Supporting Information Figures S11–S18 for ESI-MS analyses). At longer reaction times, the formation of polychlorinated species is also detected by ESI-MS. The modification in the multiplicity of the signals in the aromatic region of the ^{1}H NMR spectra (after copper removal) agrees with the substitution of a proton at the 5-position of the π rings (Figure 5).

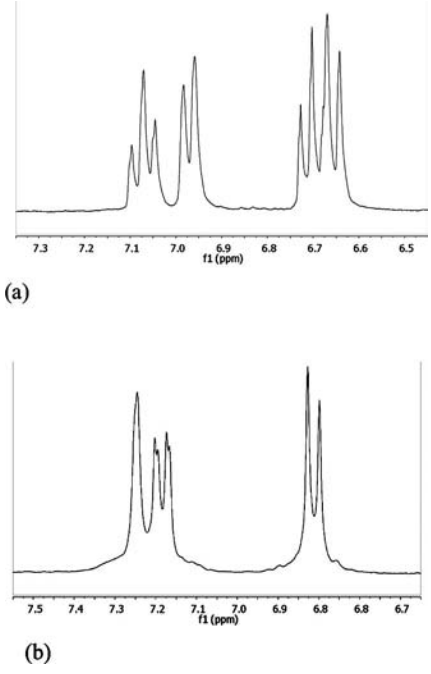

Figure 5. Aromatic regions of the ^{1}H NMR spectra of (a) starting ligand bis(2-hydroxybenzyl)-1,3-diaminopropane (H_2bhbd) and (b) the final chlorinated ligand H_2bhcbd.

Furthermore, the isotope patterns of the signals detected by ESI-MS are in agreement with the presence of two chloride atoms in the molecule (vide infra). With a M/L ratio of 1:1, the principal product obtained after 24 h reaction time is the monochlorinated ligand, as evidenced by ESI-MS measurements.

With $CuBr_2$, the formation of polybrominated species is already observed while the original ligand is still present, and a mixture of various products is obtained. Hence, the reaction carried out with copper(II) chloride is more selective and only the mono- and dichlorinated products are produced.

Ring-Closure Reaction Involving the Drying Agent eof (or mof)

An additional modification of H_2bhbd that takes place in the presence of eof (or mof) has been detected by ESI-MS spectroscopy, after the removal of copper. The expected mass peaks for the reaction mixture, after Cu^{2+} removal, are m/z = 355 (dichlorinated product + H^+), 321 (monochlorinated ligand + H^+) and 287 (original ligand). However, ESI-MS peaks are observed at m/z = 365, 331 and 297. These three values are all 10 Dalton units larger than those expected for all the species anticipated. Details of the mass spectrum for the dichlorinated product are depicted in Figure 6.

The same feature is observed for the bromination reaction in the presence of dehydrating agent. The higher mass values are ascribed to a condensation reaction between the free ligand and (m)ethylformate obtained by hydrolysis of eof or mof. The resulting six-membered ring can evolve to form a cationic stabilized species through the elimination of an (m)ethoxide molecule (Figure 7).

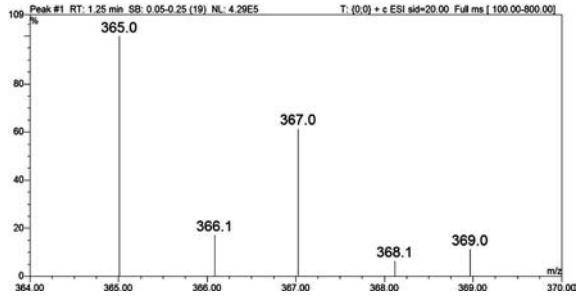

Figure 6. Enlargement of part of the ESI mass spectrum (after copper removal) obtained after reaction of copper(II) chloride with H_2bhbd at room temperature for 24 h. The isotopic pattern is in agreement with the presence of two chlorine atoms in the molecule.

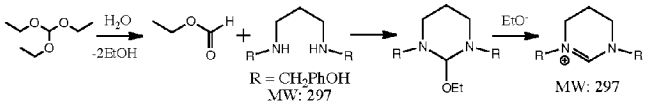

Figure 7. Proposed mechanism for the formation of the six-membered, ring-closed cationic product.

The NMR signal at 8.5 ppm found for the isolated bischlorinated ligand, i.e. after copper(II) removal and purification by chromatography, is assigned to the C–H of the ring-closed product (as has been reported also in previous studies).[23] The positive charge is delocalized between the two nitrogen atoms; hence the symmetry of the molecule is conserved, as evidenced by the NMR spectrum (see Supporting Information).

To further prove the formation of the ring-closed product, H_2bhbd has been dissolved in an acetonitrile solution containing an excess of eof (or mof). The resulting mixture has been analyzed by ESI-MS, and a weak peak is detected at m/z = 297, which corresponds to the cyclic compound. In the mass spectrum, the dominant signal belongs to the protonated ligand (286+1). When H_2bhbd reacts with an excess of ethylformate (instead of eof, triethyl orthoformate), the ESI mass spectrum shows a single peak at m/z = 297; the molecular weight peak corresponding to the original ligand is not detected. Therefore, ethylformate also allows a complete conversion of the ligand to the cyclized compound. The reaction of H_2bhbd with an excess of formaldehyde has been studied as well and a mass peak at m/z = 299 is detected. The ligand reacts with CH_2O to generate a saturated six-membered ring, as is well known in the case of 1,3-diamine in the presence of formates.[24]

As expected, with H_2bhbdi, this ring closure reaction is not observed under the above conditions as the imine groups cannot react with eof (or mof), in contrast to the N–H groups of H_2bhbd.

Bromination of H_2bhbdi Investigated by UV/Vis Spectroscopy

The modification of H_2bhbdi in the presence of copper bromide has been studied by UV/Vis spectroscopy. The formation of the monobrominated ligand leads to the disappearance of the absorption bands at 350 and 640 nm, and the formation of the dibrominated ligand is characterized by the appearance of a new band at 320 nm (Figure 8 and S19).

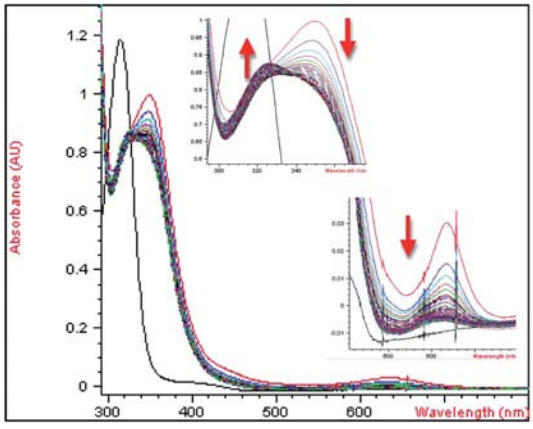

Figure 8. UV/Vis spectra for a solution of H_2bhbdi in acetonitrile (black line) monitored as a function of time after addition of $CuBr_2$. The insets show enlargements of the regions 290–400 and 400–800 nm.

The reaction rate, k_1, for the monobromination step can be determined by following the decrease in the absorbance at 340 nm (at this wavelength, i.e. the isosbestic point for the mono- to the dibrominated ligand reaction step, the absorbance changes are solely due to the formation of the copper complex of the monobrominated ligand). The data have been fitted with the classical equation for an exponential decay, Equation (4), which can be used in the case of an irreversible reaction.

$$Abs(340\text{ nm}) = Abs_{340}(\infty) + B \times \exp(-k_1 \times t) \quad (4)$$

where $Abs_{340}(\infty)$ is the residual value of absorbance at 340 nm, B is the variation of absorbance observed during the process, k_1 is the rate constant for the monosubstitution process and t is the time expressed in seconds.

The data obtained following the increase in the new band at 320 nm can be interpolated in Equation (5), which can be used to determine the value of the rate constant for the formation of the coordination compound with the dibrominated ligand.

$$Abs(320\text{ nm}) = Abs_{320}(\infty) + C \times \exp(-k_1 \times t) + D \times \exp(-k_2 \times t) \quad (5)$$

where $Abs_{320}(\infty)$ is the residual value of absorbance at 320 nm, C is the variation of absorbance for the first bromination step and D is that for the second bromination occurring with the rate constant k_2.

The fitting of the data for the reaction carried out with a M/L ratio of 3:2 (which corresponds to the ratio observed by XRD) gives values of $1.42(\pm0.03) \times 10^{-3}$ for k_1 and $2.9(\pm0.2) \times 10^{-4}$ for k_2 (Figure 9). Details for the variation of k_1 and k_2 are given in Figure S20 as a function of the concentration of the reagents.

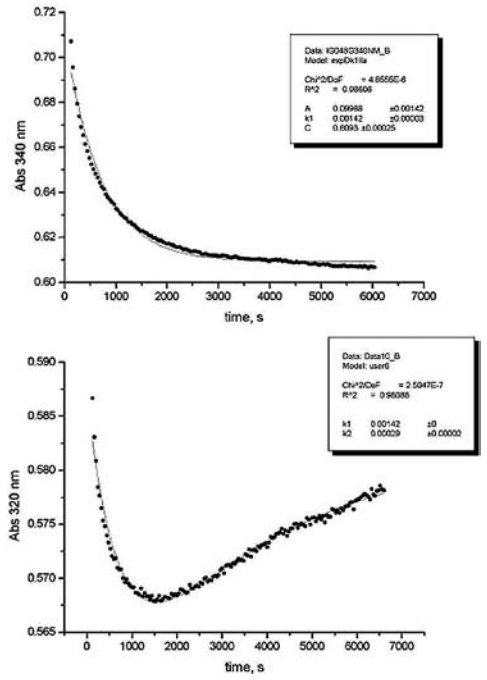

Figure 9. Representation of the fitting of the variation of (top) the absorbance at 340 nm with Equation (4) and (bottom) the absorbance at 320 nm with Equation (5).

The reaction (in the absence of eof) has been investigated by varying the ligand and $CuBr_2$ concentrations. The rate constant for the monobromination step does not change with the concentration of the ligand or $CuBr_2$.

Conclusions

The halogenation of the aromatic rings of H_2bhbd and H_2bhbdi, mediated by copper(II), occurs under extremely mild conditions, i.e. in air and at room temperature. The reaction observed in acetonitrile does not take place in methanol or dichloromethane. The precise role of the solvent has yet to be elucidated; the fact that acetonitrile is known to stabilize copper(I) species may play a role here.

The oxidative halogenation occurs with a high selectivity for the 5-position on the aromatic ring, which is also not yet understood. A possible mechanism for the selective activation of the 5-position on the aromatic ring is proposed in Figure 10. The oxidative halogenation of the phenol groups may occur through the formation of a stabilized quinonic intermediate associated with a reduction of both bridged copper(II) ions. Next, a chloride anion could selectively attack the "activated" 5-position of the aromatic ring. Subsequent rearrangement of the quinone generates the chlorinated arene.

Thus, after formation of the trinuclear copper(II) compound and deprotonation of the phenolic functional groups of H_2bhbd (**I**; Figure 10), the phenolato unit is oxidized to the corresponding phenoxonium cation, through the reduction of two copper(II) ions to a copper(I) species (**II**; Figure 10). The phenoxonium cation could then be attacked by a chloride anion (or bromide) (**III**; Figure 10), which is

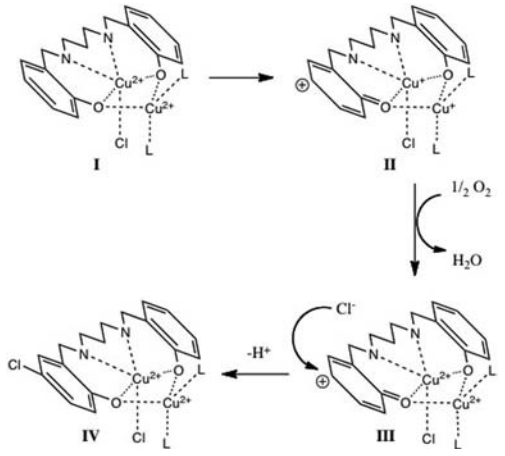

Figure 10. Proposed mechanism for the oxidative chlorination of H_2bhbd mediated by Cu^{II} and Cl^- (shown for the monochlorination step only). L can be a solvent molecule, such as CH_3CN, which is known to stabilize copper(I) species.

the rate-determining step for the reaction. The copper(I) centres are then reoxidized by dioxygen (clearly no reaction occurs in the absence of molecular oxygen, so the halogenation of the ring should occur after the reoxidation of the metal centres). Finally, through deprotonation and rearrangement, the aromatic ring is regenerated (**IV**; Figure 10).

The proposed mechanism explains the high selectivity of the nucleophilic attack of the phenolate functions on the *para* (5) carbon atom, which can be achieved through the formation of a phenoxonium cation as the key active species, as observed in related studies, i.e. in the case of the oxidative polymerization of 2,6-dimethylphenol.[25]

The formation of polyhalogenated products or C–C coupling products, which are usually observed for radical-based processes mediated by copper ions, is negligible. Moreover, no radical signal was detected by EPR spectroscopy under the experimental conditions of the present study. Nevertheless, a radical pathway cannot be excluded.

Phenoxonium cationic species are also known to be stabilized by coordination to metal ions,[26] especially in presence of dinuclear copper(II) centres.

Theoretical mechanistic studies carried out in case of the oxidative polymerization of phenols have invoked a two-electron transfer from a phenolate ligand to the metal (dinuclear Cu^{II}) to form an oxido-coordinated singlet phenoxonium cation (i.e. with a positively charged ring) and a reduced metal centre.[25b,27]

The investigation of the distribution of products in real time has allowed us to underline that the process takes place through monohalogenation steps with a high selectivity for aromatic substitution in the 5-position (more activated compared to the 3-position, which is also known to be activated).[28]

In the presence of eof (or mof), ring-closed products are generated. The original (H_2bhbd) and halogenated (mono- or bischlorinated) ligands present in solution react quantitatively with the hydrolyzed drying agent (eof or mof) to

generate six-membered ring compounds that have been identified by ESI-MS measurements.

The bromination of H_2bhbdi is observed in the trinuclear copper(II) cluster obtained in acetonitrile. Single-crystal X-ray diffraction studies show that the brominated copper compound exhibits the same structure as that observed for the chlorinated one.

UV/Vis spectroscopic studies have allowed us to determine the rate constants for the mono- and bisbromination steps. The rate constant determined for the monobromination step, k_1, is four times higher than that observed for the formation of the bisbrominated product, k_2. The observed rate constants, k_1 and k_2, do not vary with the reagent concentrations. Hydroxylated products have not been observed, at least when dry solvents were used or in the presence of a dehydrating agent (eof or mof).

Under the experimental conditions used for H_2bhbd, the ligand H_2bhbdi is not chlorinated and a dinuclear copper(II) compound is obtained; the same coordination compound is obtained in methanol and acetonitrile, which has been structurally characterized by X-ray diffraction.

Further studies are necessary to elucidate the intimate mechanism of the selective activation of the 5-position of the aromatic ring, which is still poorly understood. The comprehension of the process, through the determination of the active species involved, can lead to the development of mild, efficient and selective catalysts for halogenation reactions of aromatic functions.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. C, H, N determinations were performed with a Series II CHNS/O 2400 analyzer. ^{1}H NMR spectra were recorded with a DPX300 Bruker spectrometer. The ESI-MS measurements were carried out with a Thermo Finnigan Aqa mass detector.

Synthesis of H_2bhbdi: Bis(2-hydroxybenzyl)-1,3-diminopropane (H_2bhbdi) was prepared by condensation of salicylaldehyde and 1,3-diamine in methanol. Yield: 87%. $C_{17}H_{20}N_2O_2$ (284.36): calcd. C 71.8, H 7.09, N 9.85; found C 70.5, H 6.9, N 9.9. ESI-MS: *m*/*z* = 282.9. IR: $\tilde{\nu}$ = 3058.1, 2947.6, 2872.0, 1636.7, 1616.4, 1580.8, 1557.7, 1496.1, 1417.8, 1383.9, 1363.5, 1340.3, 1314.1, 1281.3, 1212.4, 1145.0, 1122.3, 1104.9, 1084.6, 1051.8, 1026.4, 1007.1, 974.1, 880.0, 855.0, 779.3, 749.9, 736.0, 667.8, 640.1, 571.5, 552.8, 520.3, 464.2, 404.6, 355.2, 329.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$; Me_4Si): δ = 2.11 (m, 2 H, CH_2), 3.74 (t, 4 H, CH_2), 6.81–7.32 (m, 8 H, Ph), 8.46 (s, 2 H, CH) ppm.

Synthesis of H_2bhbd: Bis(2-hydroxybenzyl)-1,3-diaminopropane (H_2bhbd) was prepared by condensation of salicylaldehyde and 1,3-diamine, followed by reduction of the imine bond in methanol with $NaBH_4$. Yield: 94%. $C_{17}H_{22}N_2O_2$ (286.37): calcd. C 71.3, H 7.7, N 9.8; found C 70.6, H 7.6, N 9.9. ESI-MS: *m*/*z* = 286.95. IR: $\tilde{\nu}$ = 3291.8, 1595.8, 1456.0, 1386.1, 1256.0, 1100.0, 1027.4, 994.4, 837.2, 751.8, 723.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$; Me_4Si): δ = 1.79 (m, 2 H, CH_2), 2.75 (t, 4 H, CH_2), 3.99 (s, 4 H, CH_2), 6.75–6.83 (m, 4 H, Ph), 6.98 (d, 2 H, Ph), 7.16 (t, 2 H, Ph) ppm.

Synthesis of $[Cu_3(bhcbd)_2Cl_2](CH_3CN)$ (1): A solution of H_2bhbd (360 mg, 1.25 mmol) in acetonitrile (15 mL) was added to a solution of $CuCl_2$ (273 mg, 2 mmol) in acetonitrile (15 mL). In both solutions, triethyl orthoformate was added (trimethyl orthoformate can also be used) to remove traces of water present in the solvent and therefore avoid the formation of partially hydroxylated products. The resulting reaction mixture was stirred in air for 24 h and subsequently filtered. Slow evaporation of the solvent led to the formation of brown crystals after 4–5 d. Yield: 13%. IR: $\tilde{\nu}$ = 3139.5, 2924.4, 2866.2, 1683.2, 1596.0, 1575.7, 1479.8, 1456.5, 1418.8, 1322.9, 1273.5, 1195.0, 1078.8, 1043.9, 1011.9, 956.7, 866.6, 753.3, 730.0, 671.9, 401.7 cm^{-1}. $C_{34}H_{32}Cl_6Cu_3N_4O_4$ (964.01): calcd. C 42.36, H 3.35, N 5.81; found C 38.72, H 3.49, N 5.24. The C, H, N analyses of the powders obtained fit with the molecular formula $C_{34}H_{32}N_4$; however, the samples contained impurities, probably copper chloride used in excess to perform the reaction.

Synthesis of $[Cu_2(bhbdi)Cl_2]$ (2): A solution of H_2bhbdi (364 mg, 1.29 mmol) in acetonitrile (15 mL) was added to a solution of $CuCl_2$ (257 mg, 1.92 mmol) in acetonitrile (15 mL). In both solutions triethyl orthoformate was added as a drying agent (trimethyl orthoformate can also be used). The resulting reaction mixture was stirred in air for 24 h and subsequently filtered. Slow evaporation of the solvent led to the formation of dark crystals after one week. Yield: 37%. $C_{17}H_{18}Cl_2Cu_2N_2O_2$: C, 42.51 H 3.78, N 5.83; found C 42.98, H 3.29, N 6.00. IR: $\tilde{\nu}$ = 354, 380, 418, 452, 538, 598, 604, 668, 686, 740, 736, 76, 856, 898, 912, 962, 960, 1038, 1070, 1074, 1104, 1154, 1198, 1220, 1286, 1346, 1404, 1436, 1476, 1548, 1594, 1616, 2820, 2898, 3012 cm^{-1}.

Synthesis of $[Cu_3(bhbrbdi)Br_2]$ (3): A solution of H_2bhbdi (368 mg, 1.30 mmol) in acetonitrile (15 mL) was added to a solution of $CuBr_2$ (574 mg, 2.58 mmol) in acetonitrile (15 mL). In both solutions, triethyl orthoformate was added as a drying agent (trimethyl orthoformate can also be used). The resulting reaction mixture was stirred in air for 3 h and subsequently filtered. Slow evaporation of the solvent led to the formation of dark crystals after 3–4 d. $C_{34}H_{24}Br_8Cu_3N_4O_4$ (bisbrominated compound): calcd. C 29.54, H 1.75, N 4.05, Br 46.24 found C 44.30, H 3.53, N 6.30, Br 18.60. Accordingly, the% of Br detected corresponds to the 2.5% of bromination. This synthesis was repeated several times, with the aim to increase and understand the degree of bromination. However, observed differences were quite small. In two cases singles crystals were obtained and analyzed as compounds **3a** and **3b**. Their composition is slightly different from **3**, and the structures are presented in the SI.

Chlorination and Bromination Reaction of H_2bhbd and H_2bhbdi: A solution of H_2bhbd (360 mg, 1.25 mmol) or H_2bhbdi (360 mg, 1.28 mmol) in acetonitrile (15 mL) was added to a solution of $CuCl_2$ (410 mg, 3 mmol) or $CuBr_2$ (682 mg, 3 mmol) in acetonitrile (15 mL). In both solutions, triethyl orthoformate was added as dehydrating agent (also trimethyl orthoformate can be used). The final solution was stirred in air for 24 h, subsequently filtered and analyzed by ESI-MS.

Extraction of the Ligand: A solution of H_2bhbd (360 mg, 1.25 mmol) in acetonitrile (15 mL) was added to a solution of $CuCl_2$ (410 mg, 3 mmol) in acetonitrile (15 mL). In both solutions, triethyl orthoformate was added as dehydrating agent (also trimethyl orthoformate can be used). After 24 h of reaction, a 10 mL sample of the reaction mixture was treated with excess aqueous Na_2S (4 equiv.), producing a black precipitate after partial solvent removal from the CH_3CN phase. The solid material was removed by filtration, and the filtrate was extracted into dichloromethane. The dried organic phase was characterized by ^{1}H NMR and ESI-MS spectroscopy. $C_{17}H_{20}Cl_2N_2O_2$ (355.26): calcd. C 57.47, H 5.67, N 7.89, Cl 19.96; found C 48.76, H 4.81, N 6.26, Cl 18.4. The C,

H, N analyses fit with the formula $C_{18}H_{21}Cl_2N_2O_2$, ascribed to the ring-closed product. Moreover, these analyses suggest the presence of remaining Na_2S salts. ESI-MS: 365.01 (in the presence of dehydrating agent, 356.04 under dry solvent conditions) IR: $\tilde{\nu}$ = 3291.5, 2924.4, 2866.2, 1683.2, 1596.0, 1575.7, 1479.8, 1456.5, 1322.9, 1273.5, 1241.5, 1195.0, 1151.4, 1078.8, 1043.9, 1011.9, 956.7, 866.6, 753.3, 730.0, 671.9, 581.8, 401.7 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$; Me_4Si): δ = 1.92 (m, 2 H, CH_2), 3.27 (t, 3 H, CH_2), 4.59 (s, 4 H, CH2), 6.82 (d, 2 H, Ph), 7.20 (d, 2 H, Ph), 7.26 (s, 1 H, Ph) ppm.

Bromination of H_2bhbdi Investigated by UV/Vis Spectroscopy: A typical experiment is as follows: $CuBr_2$ (0.180 μmol) was added to a solution of H_2bhbdi (2 mL CH_3CN, 0.128 μmol, 0.064 mM). The reaction mixture was monitored by UV/Vis spectroscopy for 2.5 h, recording one spectrum every 30 s (between 180–1000 nm). This investigation was carried out with different $CuBr_2$ concentrations (in the range 0.022–0.112 mM), as well as various concentrations of H_2bhbdi (between 0.016 and 0.096 mM).

X-ray Crystallographic Analysis and Data Collection: Crystallographic data and refinement details are given in Table 1. A single crystal was selected for the X-ray measurements and mounted to the glass fiber using the oil drop method,[29] and data were collected at 173(2) K with a Nonius Kappa CCD diffractometer (Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). The intensity data were corrected for Lorentz and polarization effects and for absorption. The programs COLLECT,[30] SHELXS-97,[31] and SHELXL-97[32] were used for data reduction, structure solution, and structure refinement, respectively. The non-hydrogen atoms were refined anisotropically. The H atoms were geometrically fixed and allowed to ride on the parent atoms. CCDC-815974 (for **1**), -815975 (for **2**), -815976 (for **3**), -815972 (for **3a**) and -815973 (for **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the X-ray structures of the compounds and NMR, UV/Vis and ESI mass spectra.

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