The Role of the Apical Donor in the Decomposition of Copper(II) Benzoate under DOW-Phenol Conditions

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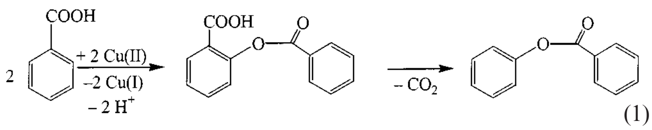
The synthesis and characterization of copper(II) benzoates with the apical donors pyridine, 2-CH_3-pyridine, 2,4-$(CH_3)_2$-pyridine, 2,6-$(CH_3)_2$-pyridine, 2-fluoropyridine, 2-chloropyridine, 2-bromopyridine, 3-bromopyridine, 2,5-dibromopyridine, 3,5-dibromopyridine, and aniline, starting from copper(II) benzoate, is reported. Single-crystal X-ray structures of the products with four apical ligands show the usual paddle-wheel structure of copper(II) carboxylates; in the case of aniline no paddle-wheel dicopper(II) benzoate could be isolated. The products of thermal decomposition of the pure copper(II) compounds were analyzed by HPLC, LC-MS, and GCFID, and the expected DOW-phenol products were found in all cases other than that of aniline. This supports the assumption that a paddle-wheel dicopper(II) benzoate is required for the DOW-phenol reaction. Generally, high *ortho*-selectivities (to phenyl benzoate and phenol; the selectivity increases with increasing basicity) are obtained, in good agreement with earlier findings on the role of the base. Small but significant steric effects are observed in the series of methylated pyridine donors and the monohalogenated pyridine donors used as apical ligands; with the two dibromopyridine donors there are large steric effects and the DOW-phenol reaction is partially suppressed. With halogenated pyridine donors as apical ligands, a Cu^{I}-catalyzed process occurs, leading to dehalogenation.

Introduction

The selective oxidation of hydrocarbons in the liquid phase is a major challenge in fundamental and applied research.[1−3] Generally, free-radical chain mechanisms dominate, and only in a few cases (xylene and toluene derivatives) is a high selectivity towards the corresponding acids obtained. Various approaches have been proposed to overcome these problems but, so far, these have led to only limited success. We have tried to avoid unselective free-radical chain oxidation reactions by adopting an approach that utilizes oligonuclear metal complexes in the oxygenation of hydrocarbons. The starting point for our studies was the DOW-phenol process. This converts benzoic acid into phenol under copper(II) catalysis and this reaction may be considered as a regioselective hydroxylation.[4] In the DOW-phenol process (Scheme 1), benzoic acid is oxidized at $T >$ 180 °C with moist air and copper(II) to give phenyl benzoate and CO_2; the reduced copper(I) is reoxidized by dioxygen; hydrolysis of the phenyl benzoate then yields the desired phenol and benzoic acid [Equations (1)−(5)].[4]



(1)

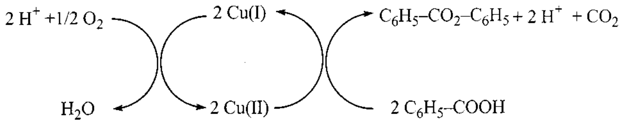
$$2\,Cu^{II} + 2\,ArCOOH \rightarrow ArCO_2Ar + 2\,H^+ + CO_2 + 2\,Cu^{I} \qquad (2)$$

$$2\,Cu^{I} + 1/2\,O_2 + 2\,H^+ \rightarrow 2\,Cu^{II} + H_2O \qquad (3)$$

$$ArCO_2Ar + H_2O \rightarrow ArOH + ArCOOH \qquad (4)$$

Overall:

$$ArCOOH + 1/2\,O_2 \rightarrow ArOH + CO_2 \qquad (5)$$



Scheme 1

The main reaction in the catalytic process (Scheme 1) is the thermal decomposition of copper(II) benzoate to *o*-benzoyloxybenzoic acid. Rapid decarboxylation leads to phenyl benzoate [Equation (1)]. The amount of CO_2 produced is directly proportional to the amount of copper(II) involved in the stoichiometric decomposition and its quantification can be used to study the kinetics of the process. Phenyl benzoate is hydrolyzed with steam to yield phenol [Equation (4)]. The overall reaction is sensitive to solvents. In anhydrous benzoic acid solutions, the *ortho*-selectivity of the benzoyloxybenzoic acid formation is only about 50% (45% *meta*-benzoyloxybenzoic acid, 5% *para*-benzoyloxybenzoic acid).[5]

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Table 1. Overview of the results of the thermal decomposition of copper(II) benzoates with substituted pyridines and aniline at 230 °C with various apical ligands

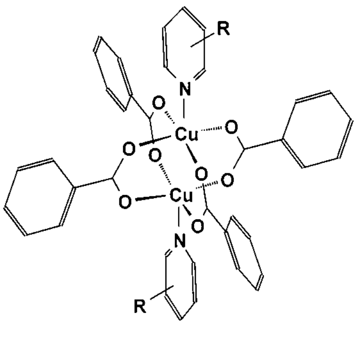
Apical donor	Conversion[a] (%)	DOW Phenol product (%)[b] *ortho*	*meta*	*para*	Reduced (%)[b]	Benzene (%)[c]
pyridine	40.9	99.9	0.1	–	–	–
2-CH_3-pyridine	12.4	98.5	1.3	0.2	–	–
2,4-$(CH_3)_2$-pyridine	6.6	97.8	1.8	0.4	–	–
2,6-$(CH_3)_2$-pyridine	3.8	95.7	3.5	0.8	–	1.3
aniline	0.7[d]	93.9	5.2	0.9	–	4.0
2-F-pyridine[e]	17.7	89.2	5.6	5.2	–	8.8
2-Cl-pyridine	31.4	94.8	2.7	2.5	4.5	–
2-Br-pyridine	21.5	95.1	2.5	2.4	1.4	–
3-Br-pyridine	59.3	98.1	1.3	0.6	14.3	–
2,5-Br_2-pyridine	4.1	66.7	31.0	2.3	3.3[f]	–
3,5-Br_2-pyridine	11.6	99.2	0.8	–	12.0[g]	–

[a] With respect to copper benzoate. – [b] Reduced products in mol % copper benzoate (dimer). – [c] mol % relative to the total benzoic acid in the starting material. – [d] Most likely due to the salicylic acid reaction; aniline was completely converted to *N*-phenyl benzamide (HPLC and LC-MS). – [e] Results obtained at 250 °C; no reaction occurred at 230 °C. – [f] Products: 2-benzoyloxypyridine, 2-hydroxypyridine (approx. 1:1). – [g] Products: pyridine, 3-benzoyloxypyridine, 3-hydroxypyridine (approx. 2:2:1.5).

Results and Discussion

Thermal Decomposition of Copper(II) Benzoate with Substituted Pyridine Donors or Aniline at the Apical Sites of the Paddle-Wheel Dicopper(II) Compounds

The influence of substituted pyridine donors bearing electron-withdrawing or electron-donating groups was studied to investigate the role of the donors at the apical sites of the paddle-wheel dicopper(II) complexes in the DOW-phenol process (see Scheme 2). Copper(II) benzoate with various pyridine donors (different substitution patterns) and with aniline was pyrolyzed in a sealed silica tube (stoichiometric reaction; see Exp. Sect.). Table 1 summarizes the identified DOW-phenol products recovered following the pyrolyses of the copper(II) compounds.



Scheme 2

An important observation is that all the apical donors studied show high *ortho*-selectivities, except for 2,5-dibromopyridine. This is in line with earlier observations on the effect of base in the DOW-phenol reaction.[5] In the series pyridine, 2-methylpyridine, 2,4-dimethylpyridine, and 2,6-dimethylpyridine, both the conversion and the *ortho*-selectivity decrease, from 40.9% to 3.8% and from 99.9% to 95.7%, respectively. Since the basicity in this series of pyridines follows the order pyridine < 2-methylpyridine < 2,4-dimethylpyridine ≈ 2,6-dimethylpyridine, both the conversion and the *ortho*-selectivity might have been expected to increase, as was observed with Mg^{II} benzoate.[5] However, the pyridine donors coordinate to Cu^{II} whereas Mg^{II} benzoate merely acts as a simple base. The electronic effect of the pyridine donors influences the thermal stability and hence the reactivity: the more electron-donating the pyridine donor is, the less effectively Cu^{II} will be able to abstract electrons from benzoate. If, however, the electrophile resulting from a benzoate is formed, the steric effect of the methylated pyridine donors may slightly decrease the probability of an *ortho*-attack at the corresponding pyridinium benzoate.

The halogenated pyridine donors constitute another interesting series. Unfortunately, their conversion cannot be compared directly with that of the methylated pyridine donors because they are also subject to reduction, which produces additional Cu^{II}.[6] This reaction seems to be comparable to the reduction of halogenated hydrocarbons.[7] The scope and limitations of the catalytic reduction are reported separately.[6]

The use of 2-fluoropyridine did not lead to any reaction at 230 °C. However, at 250 °C a fast substitution reaction of benzoate on the fluoride was observed prior to the DOW-phenol reaction. The resulting *ortho*-selectivity of approximately 89% cannot be assigned to 2-fluoropyridine, but mainly to 2-benzoyloxypyridine and HF instead.[6]

The other halogenated pyridine donors show *ortho*-selectivities of 66.7% (2,5-dibromopyridine), 94.8% (2-chloropyridine), 95.1% (2-bromopyridine), 98.1% (3-bromopyridine), and 99.2% (3,5-dibromopyridine). We believe that in these cases, both electronic and steric effects play a similar role to that observed with the methylated pyridine donors, albeit to a less pronounced extent. Despite the increasing size of the substituents, a chloro or a bromo substituent in the 2-position of the pyridine has a similar effect on the *ortho*-selectivity as two methyl groups in the 2,6-positions. This might be due to the fact that only one side of the benzoate in a pyridinium benzoate is accessible for the coupling reaction. Moreover, a bromo substituent in the 3-position of pyridine has a similar effect as a methyl group in the 2-position. Comparing the pyridine donors with two bromo substituents in the 2,5- and 3,5-positions, a large steric effect on the *ortho*-selectivity due to the second bromine in the 2-position is evident.

For the series of monohalogenated pyridine donors, the relative amount of reduced material (given as mol % of additional copper benzoate; see Table 1) is comparatively small with respect to the observed conversion, but it is high for the dibromopyridine donors. For the latter, this correlates with the observed conversion ratios. The total conversion may therefore be interpreted as follows. The steric demand of dibromo-substituted pyridine donors in the apical positions leads to a slow DOW-phenol reaction; the resulting Cu^{I} leads to a comparably high reduction and substitution rate to yield reduced and substituted pyridine donors and Cu^{II}; the DOW-phenol reaction then also proceeds with pyridine and benzoate-substituted pyridines. The observed selectivities for the two dibromopyridine ligands support this. With 3,5-dibromopyridine, a comparatively large amount of pyridine is formed and the observed *ortho*-selectivity is 99.2%, similar to that seen with pyridine itself. With 2,5-dibromopyridine, the major product is a pyridine substituted at the 2-position and reduced at the 5-position. This secondary ligand still leads to substantial steric hindrance, and the resulting *ortho*-selectivity of 66.7% is close to that observed for Cu^{II} benzoate in the absence of base and water.[5]

The apical donor aniline blocks the DOW-phenol reaction completely. Phenyl benzoate was not detected. Instead, the quantitative formation of *N*-phenyl benzamide was observed. Since this co-elutes with phenyl benzoate in the HPLC procedure used, LC-MS, including a peak purity check, was applied to enable a quantitative determination. On adding pyridine donors to a Cu^{II} benzoate solution in acetone, the paddle-wheel structure remained intact, whereas with aniline a distinct color change was observed and no paddle-wheel dicopper(II) compound could be isolated. The failure to observe DOW-phenol chemistry with aniline supports the interpretation that paddle-wheel structures of copper(II) benzoate are a requirement for the DOW-phenol reaction.[5]

With three donors, namely 2,6-dimethylpyridine, aniline, and 2-fluoropyridine, benzene was detected as an additional product of the stoichiometric DOW-phenol reactions. Benzene is a common by-product in the DOW-phenol process, but its formation is generally attributed to Cu^{I}, reaction at the reactor wall, and high temperatures (≥ 250 °C). However, in the three cases where benzene was found (Table 1), $[Cu^{I}]$ is low and no metal reactor wall was present. With 2,6-dimethylpyridine and aniline, the reaction temperature was as low as 230 °C. Therefore, apart from in the case of 2-fluoropyridine, our interpretation of the benzene production is that a relatively strong base must be present.[8] In the case of 2-fluoropyridine, the elevated temperature might be the most important factor.

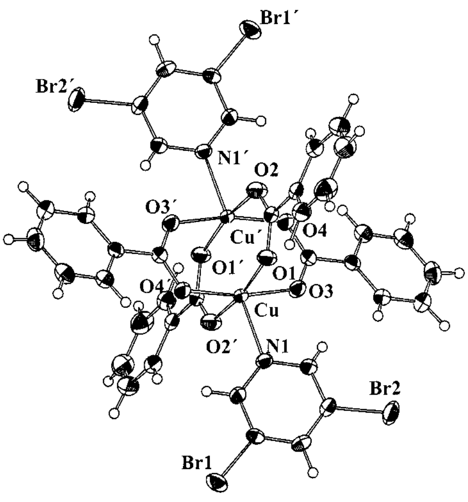


Figure 1. ORTEP[12] plot of $[Cu_2(\mu\text{-}O_2C-C_6H_5)_4(3,5\text{-}Br-C_5H_3N)_2]$ (compound **1**)

Molecular Structures of Copper(II) Benzoates with Apical Donors

For all the apical donors studied, except for aniline, dicopper(II) species with stoichiometries in agreement with the expected paddle-wheel structures were isolated. The X-ray crystal structures of the four structurally characterized dicopper(II) benzoates (see Figure 1, Table 2) are essentially identical and, as expected for copper(II), do indeed represent paddle-wheel compounds. They consist of centrosymmetric dicopper(II) units, in which each copper(II) ion is coordinated by four oxygen atoms of the four bridging carboxylate groups (see Figure 1, Scheme 2, and Table 2). The copper−copper distances range from 2.626 Å to 2.678 Å. The angle between the two planes through the two copper(II) centers and two benzoates ranges from 88.92° to 89.80°. The two pyridine rings are parallel, except in compound **2**, where their ring planes intersect at an angle of 79.23°. No paddle-wheel-type copper(II) benzoate could be isolated with aniline. Aniline seems to destroy the copper(II) benzoate fragment and this leads to the formation of unidentified mononuclear copper(II) species.

CO_2 Measurements

The pyrolyses of copper(II) benzoate in sealed silica tubes in the absence of oxygen, with all the pyridine derivatives used in this study, produce CO_2. The cumulative formation of CO_2 as a function of time with copper(II) benzoate alone reaches a constant value of approximately 66% with respect to the stoichiometrically expected amount (Figure 2; approximately 50% *o*-selectivity in the formation of the benzoyloxybenzoic acid, see above[5]). With the methylated and halogenated pyridine donors, the production of CO_2 increases significantly [see Figure 2; with pyridine 109% and with 3-bromopyridine 108% was obtained; 100% CO_2

Table 2. Selected distances [Å] and angles [deg.] for tetrakis(benzoato-µ-*O*,*O′*)bis(3,5-dibromopyridine)dicopper(II) (compound **1**), tetrakis(benzoato-µ-*O*,*O′*)bis(3-bromopyridine)dicopper(II) (compound **2**), tetrakis(benzoato-µ-*O*,*O′*)bis(2,5-dibromopyridine)dicopper(II) (compound **3**), and tetrakis(benzoato-µ-*O*,*O′*)bis(2-chloropyridine)dicopper(II) (compound **4**)

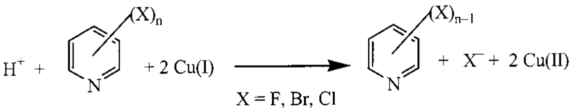
Selected bond lengths [Å]	Compound **1**	Compound **2**	Compound **3**	Compound **4**
Cu...Cu′	2.6264(6)	2.6775(6)	2.6585(8)	2.6475(6)
Cu-N1	2.206(2)	2.176(3)	2.262(3)	2.235(9)
Cu′-N1′	2.206(2)	2.159(3)	1.966(2)	2.214(10)
Cu-O1	1.9615(19)	1.947(3)	1.958(2)	1.960(2)
Cu-O2′	1.9748(19)	1.952(2)	1.976(2)	1.970(2)
Cu-O3	1.9624(19)	1.979(2)	1.960(2)	1.961(2)
Cu-O4′	1.9633(19)	2.034(2)	1.951(2)	1.963(2)
Cu′-O1′	1.9615(19)	2.018(2)	1.958(2)	1.960(2)
Cu′-O2	1.9748(19)	1.965(2)	1.976(2)	1.970(2)
Cu′-O3′	1.9624(19)	1.945(2)	1.960(2)	1.961(2)
Cu′-O4	1.9633(19)	1.952(3)	1.951(2)	1.963(2)
Selected valence angles [deg]				
O1-Cu-O4′	89.15(8)	90.20(11)	89.70(11)	89.92(10)
O4′-Cu-O2′	88.83(8)	90.16(11)	87.86(11)	89.80(12)
O2′-Cu-O3	90.82(9)	87.48(11)	89.22(11)	88.49(11)
O3-Cu-O1		89.99(11)	90.51(11)	89.28(9)
O1′-Cu′-O4		88.39(11)		
O4-Cu′-O2		90.40(11)		
O2-Cu′-O3′		89.47(11)		
O3′-Cu′-O1′		89.94(11)		
O1-Cu-N1	100.77(8)	93.83(12)	104.57(10)	97.7(4)
O4′-Cu-N1	94.75(8)	86.14(11)	101.07(10)	87.8(3)
O2′-Cu-N1	90.41(8)	92.48(11)	88.17(10)	97.0(4)
O3-Cu-N1	96.66(8)	114.20(12)	90.82(10)	104.2(3)
O1′-Cu′-N1′		88.03(10)		95.1(4)
O4-Cu′-N1′		93.43(11)		95.3(4)
O2-Cu′-N1′		111.53(11)		94.3(4)
O3′-Cu′-N1′		91.62(11)		96.7(4)
O1-Cu-Cu′	89.14(6)	84.56(8)	87.79(7)	83.69(6)
Ó4-Cu-Cu′	83.86(6)	86.05(8)		
O2′-Cu-Cu′	79.66(6)	89.34(7)	79.66(8)	84.28(7)
O3-Cu-Cu′	84.85(6)	81.17(8)		85.52(6)
O1′-Cu′-Cu		77.80(7)		
Ó4′-Cu-Cu′		78.54(7)	88.88(7)	82.53(7)
O2-Cu′-Cu		82.63(7)		
O3′-Cu′-Cu		88.60(7)	78.80(7)	
N1-Cu-Cu′		164.58(9)	164.02(8)	177.4(4)
N1′-Cu′-Cu		165.83(8)		170.2(3)

corresponds to the stoichiometric amount of copper(I) generated in one reduction cycle (see Scheme 1)].

There are various explanations for this behavior. An important observation is that after the pyrolysis with pyridine, elemental copper is found in the reaction vessel. This indicates that copper(I), formed during the reduction of the halogenated pyridines and the ensuing DOW-phenol process, undergoes disproportionation to copper(0) and copper(II) [Equation (6)]. The resulting copper(II) leads to additional CO_2 production [Equation (1) and Scheme 1].

$$2\,Cu^{I} \rightarrow Cu^{0} + Cu^{II} \qquad (6)$$

Moreover, pyridine catalyzes the decarboxylation of aromatic acids.[8] The copper(II) compound with 3-bromopyridine leads to an even larger excess of CO_2, although no elemental copper could be found after the reaction. This may be related to the detection of reduced pyridines by HPLC. After the usual decomposition of copper(II) benzoate, copper(I) is re-oxidized to copper(II) by the halopyridines [Equation (7)]. The complete reduction of halogenated pyridine derivatives in a catalytic reaction is prohibited by the precipitation of copper(I) halides.[7] These processes are described in detail in a separate publication.[6]



(7)

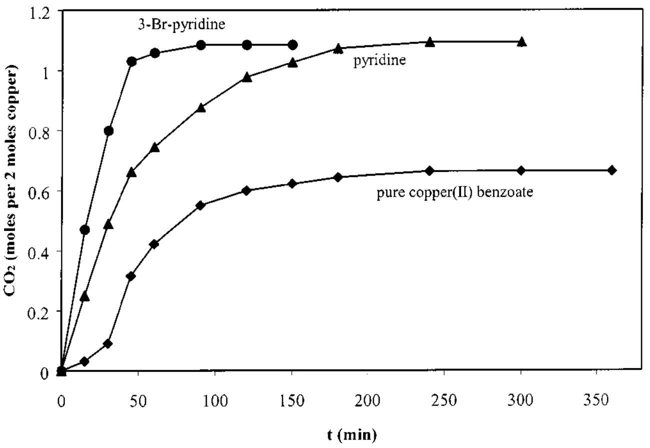


Figure 2. Cumulative CO_2 formation during the pyrolysis of various copper(II) benzoates with apical donors (stoichiometric reaction under argon; for conditions, see Exp. Sect.)

Experimental Section

Materials: Copper(II) benzoate was obtained from DSM and was used without purification. All other compounds were purchased from Sigma or Aldrich and were used without further purification. The purity ranges were 97−99%.

Syntheses of the Copper(II) Compounds

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(3,5\text{-Br}-C_5H_3N)_2]$ (1): 3,5-Dibromopyridine (1.00 g, 4.22 mmol) was added to a solution of copper(II) benzoate (1.37 g, 2.12 mmol) in dry acetone (50 mL). After 24 h, the turquoise-green precipitate was collected by filtration, washed with Et_2O, and dried in vacuo. Yield: 1.55 g (67.4%). − IR (KBr): $\tilde{\nu}$ = 3060 [ν(C−H)], 1626 [ν(C=N)], 1600 [ν(C=C)], 1574 [$\nu_{asym.}$ (C=O, COO^-)], 1406 [$\nu_{sym.}$ (C=O, COO^-)], 1022 [ν(aryl-Br)] cm^{-1}. − $C_{38}H_{26}Br_4Cu_2N_2O_8$ (1085.34): calcd. C 42.03, H 2.41, N 2.58; found C 42.09, H 2.61, N 2.51.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(3\text{-Br}-C_5H_4N)_2]$ (2): 3-Bromopyridine (1.50 g, 9.81 mmol) was added to a solution of copper(II) benzoate (2.05 g, 3.17 mmol) in dry acetone (50 mL). The reaction mixture was heated at 60 °C for 24 h. The turquoise-green precipitate was then collected by filtration, washed with Et_2O, and dried in vacuo. Yield: 2.13 g (72.4%). − IR (KBr): $\tilde{\nu}$ = 3066 [ν(C−H)], 1628 [ν(C=N)], 1616 [ν(C=C)], 1572 [$\nu_{asym.}$ (C=O, COO^-)], 1402 [$\nu_{sym.}$ (C=O, COO^-)], 1028 [ν(aryl-F)] cm^{-1}. − $C_{38}H_{28}Cu_2Br_2N_2O_8$ (927.54): calcd. C 49.21, H 3.04, N 3.02, Br 17.23; found C 49.19, H 3.37, N 2.87, Br 16.47.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(2,5\text{-Br}-C_5H_3N)_2]$ (3): 2,5-Dibromopyridine (2.00 g, 8.44 mmol) was added to a solution of copper(II) benzoate (2.74 g, 4.43 mmol) in dry acetone (50 mL). The reaction mixture was heated at 60 °C for 24 h. The solvent was then removed under reduced pressure, and the residue was washed with petroleum ether (30 mL) and dried in vacuo. Yield: 2.59 g (56.3%). − IR (KBr): $\tilde{\nu}$ = 3063 [ν(C−H)], 1625 [ν(C=N)], 1600 [ν(C=C)], 1570 [$\nu_{asym.}$ (C=O, COO^-)], 1410 [$\nu_{sym.}$ (C=O, COO^-)], 1070 [ν(aryl-Br)] cm^{-1}. − $C_{38}H_{26}Br_4Cu_2N_2O_8$ (1085.34): calcd. C 42.03, H 2.41, N 2.58, Br 29.45; found C 42.48, H 2.72, N 2.57, Br 28.50.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(2\text{-Cl}-C_5H_4N)_2]$ (4): 2-Chloropyridine (2.00 g, 17.61 mmol) was added to a solution of copper(II) benzoate (3.71 g, 5.72 mmol) in dry acetone (100 mL). The reaction mixture was heated at 60 °C for 24 h. The solvent was then removed under reduced pressure, and the residue was washed with petroleum ether (30 mL) and dried in vacuo. Yield: 2.46 g (51.25%). − IR (KBr): $\tilde{\nu}$ = 3062 [ν(C−H)], 1626 [ν(C=N)], 1616 [ν(C=C)], 1572 [$\nu_{asym.}$ (C=O, COO^-)], 1406 [$\nu_{sym.}$ (C=O, COO^-)], 1270 [ν(aryl-Cl)] cm^{-1}. − $C_{38}H_{28}Cu_2Cl_2N_2O_8$ (838.65): calcd. C 54.42, H 3.37, N 3.34; found C 54.48, H 3.50, N 3.13.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(2\text{-Br}-C_5H_4N)_2]$: 2-Bromopyridine (2.70 g, 17.09 mmol) was added to a solution of copper(II) benzoate (5.00 g, 7.72 mmol) in dry acetone (100 mL). The reaction mixture was heated to 60 °C for 24 h. The solvent was then removed under reduced pressure, and the residue was washed with petroleum ether (30 mL) and dried in vacuo. Yield: 4.7 g (65.64%). − IR (KBr): $\tilde{\nu}$ = 3063 [ν(C−H)], 1625 [ν(C=N)], 1600 [ν(C=C) =], 1570 [$\nu_{asym.}$ (C=O, COO^-)], 1410 [$\nu_{sym.}$ (C=O, COO^-)], 1070 [ν(aryl-Br)] = cm^{-1}. − $C_{33}H_{24}BrCu_2NO_8$ (769.55): calcd. C 51.50, H 3.14, N 1.82, Br 10.38; found C 51.52, H 3.46, N 1.84, Br 10.11.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(2\text{-F}-C_5H_4N)_2]$: 2-Fluoropyridine (1.00 g, 10.30 mmol) was added to a solution of copper(II) benzoate (2.34 g, 5.16 mmol) in dry acetone (50 mL). The reaction mixture was heated at 60 °C for 24 h. The solvent was then removed under reduced pressure, and the residue was washed with petroleum ether (30 mL) and dried in vacuo. Yield: 2.53 g (53.73%). − IR (KBr): $\tilde{\nu}$ = 3070 [ν(C−H)], 1628 [ν(C=N)], 1610 [ν(C=C)], 1574 [$\nu_{asym.}$ (C=O, COO^-)], 1404 [$\nu_{sym.}$ (C=O, COO^-)], 1270 [ν(aryl-F)] cm^{-1}. − $C_{38}H_{28}Cu_2F_2N_2O_8$ (805.74): calcd. C 56.64, H 3.50, N 3.48; found C 56.58, H 3.87, N 3.10.

$[Cu(\mu_2\text{-}O_2C-C_6H_5)_2(H_2N-C_6H_5)]_n$: To a suspension of copper(II) benzoate (1.00 g, 1.54 mmol) in petroleum ether (30 mL) was added aniline (0.29 g, 3.11 mmol). After 24 h, the green precipitate was collected by filtration, washed with Et_2O, and dried in vacuo. Yield: 1.10 g (80.65%). − IR (KBr): $\tilde{\nu}$ = 3312 [ν(N−H)], 3066 [ν(C−H)], 1596 [ν(C=C)], 1548 [$\nu_{asym.}$ (C=O, COO^-)], 1490 [$\nu_{sym.}$ (C=O, COO^-)] cm^{-1}. − $C_{40}H_{34}Cu_2N_2O_8$ (797.81): calcd. C 60.22, H 4.30, N 3.51; found C 59.16, H 4.59, N 3.72.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(C_5H_5N)_2]$: Pyridine (1.22 g, 15.42 mmol) was added to a solution of copper(II) benzoate (5.00 g, 7.72 mmol) in dry acetone (100 mL). The reaction mixture was heated at 60 °C for 24 h. The green precipitate was then collected by filtration, washed with EtOH, and dried in vacuo. Yield: 3.6 g (60.60%). − IR (KBr): $\tilde{\nu}$ = 3063 [ν(C−H)], 1628 [ν(C=N)], 1600 [ν(C=C)], 1572 [$\nu_{asym.}$ (C=O, COO^-)], 1405 [$\nu_{sym.}$ (C=O, COO^-)] cm^{-1}. − $C_{38}H_{30}Cu_2N_2O_8$ (769.76): calcd. C 59.29, H 3.93, N 3.64; found C 59.05, H 4.01, N 3.43.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4(2\text{-}CH_3-C_5H_4N)_2]$: 2-Methylpyridine (1.44 g, 15.44 mmol) was added to a solution of copper(II) benzoate (5.00 g, 7.72 mmol) in dry acetone (100 mL). The reaction mixture was heated at 60 °C for 24 h. The green precipitate was then collected by filtration, washed with Et_2O, and dried in vacuo. Yield: 3.55 g (57.63%). − IR (KBr): $\tilde{\nu}$ = 3066 [ν(C−H)], 2932 [ν(C−H, CH_3)], 1630 [ν(C=N)], 1600 [ν(C=C)], 1574 [$\nu_{asym.}$ (C=O, COO^-)], 1404 [$\nu_{sym.}$ (C=O, COO^-)] cm^{-1}. − $C_{40}H_{34}Cu_2N_2O_8$ (797.81): calcd. C 60.22, H 4.30, N 3.51; found C 60.27, H 4.38, N 3.46.

$[Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4\{2,4\text{-}(CH_3)_2-C_5H_3N\}_2]$: 2,4-Dimethylpyridine (1.65 g, 15.44 mmol) was added to a solution of copper(II) benzoate (5.00 g, 7.72 mmol) in dry acetone (100 mL). The reaction mixture was heated at 60 °C for 24 h. The green precipitate was then collected by filtration, washed with Et_2O, and dried in vacuo.

Table 3. Crystallographic data for tetrakis(benzoato-μ-*O*,*O*′)bis(3,5-dibromopyridine)dicopper(II) (compound **1**), tetrakis(benzoato-μ-*O*,*O*′)bis(3-bromopyridine)dicopper(II) (compound **2**), tetrakis(benzoato-μ-*O*,*O*′)bis(2,5-dibromopyridine)dicopper(II) (compound **3**), and tetrakis(benzoato-μ-*O*,*O*′)bis(2-chloropyridine)dicopper(II) (compound **4**)

Compound	1	2	3	4
Empirical formula	$C_{38}H_{26}Br_4Cu_2N_2O_8$	$C_{38}H_{28}Br_2Cu_2N_2O_8$	$C_{38}H_{26}Br_4Cu_2N_2O_8$	$C_{38}H_{28}Cl_2Cu_2N_2O_8$
Molecular mass	1085.33	927.52	1085.33	838.60
Crystal size [mm^3]	0.48 x 0.40 x 0.20	0.27 x 0.23 x 0.22	0.28 x 0.24 x 0.09	0.48 x 0.34 x 0.16
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
space group	P-1	$P2_1/c$	P-1	$P2_1/n$
a (Å)	10.1935(2)	17.5158(2)	10.0911(1)	10.3650(2)
b (Å)	10.6326(1)	10.5161(1)	10.2947(1)	10.3761(1)
c (Å)	10.6556(2)	19.9834(2)	19.2761(3)	17.1173(2)
α (deg)	64.091(1)	90	97.216(1)	90
β (deg)	81.185(1)	97.423(1)	92.919(1)	100.073(1)
γ (deg)	68.511(1)	90	106.133(1)	90
V (Å^3)	966.57(3)	3650.05(7)	1900.64(4)	1812.56(4)
Z	1	4	2	2
Reflections collected / unique (Rint)	11640 / 4639 (0.027)	49013 / 8983 (0.049)	23541 / 8991 (0.039)	18358 / 4413 (0.046)
Density$_{calcd.}$ [g cm^{-3}]	1.865	1.688	1.896	1.537
Absorption coefficient [mm^{-1}]	5.288	3.410	5.378	1.376
F(000)	530	1848	1060	852
Goodness-of-fit on	0.987	1.047	0.977	1.062
$R1$ [I>2σ(I)]	0.0332	0.0458	0.0342	0.0472
$wR2$ (all data)	0.0886	0.1361	0.0901	0.1484
Largest diff. peak and hole [e /Å^{-3}]	0.797 / -0.671	1.919 / -2.402	0.899 / -1.199	0.630 / -0.646

Yield: 2.60 g (40.76%). − IR (KBr): $\tilde{\nu}$ = 3062 [ν(C−H)], 2928 [ν(C−H, CH_3)], 1632 [ν(C=N)], 1598 [ν(C=C)], 1574 [$\nu_{asym.}$ (C=O, COO^-)], 1402 [$\nu_{sym.}$ (C=O, COO^-)] cm^{-1}. − $C_{42}H_{38}Cu_2N_2O_8$ (825.86): calcd. C 61.08, H 4.64, N 3.39; found C 60.97, H 4.62, N 3.24.

[$Cu_2(\mu_2\text{-}O_2C-C_6H_5)_4\{2,6\text{-}(CH_3)_2-C_5H_3N\}_2$]: 2,6-Dimethylpyridine (1.65 g, 15.44 mmol) was added to a solution of copper(II) benzoate (5.00 g, 7.72 mmol) in dry acetone (100 mL). The reaction mixture was heated at 60 °C for 24 h. The solvent was then removed under reduced pressure, and the residue was washed with petroleum ether (30 mL) and dried in vacuo. Yield: 3.24 g (58.38%). − IR (KBr): $\tilde{\nu}$ = 3062 [ν(C−H)], 2928 [ν(C−H, CH_3)], 1632 [ν(C=N)], 1598 [ν(C=C)], 1574 [$\nu_{asym.}$ (C=O, COO^-)], 1402 [$\nu_{sym.}$ (C=O, COO^-)] cm^{-1}. − $C_{35}H_{29}Cu_2NO_8$ (718.52): calcd. C 58.50, H 4.68, N 1.95; found C 58.69, H 4.63, N 1.98.

Pyrolyses: The pure copper(II) benzoate salts with the apical donors (150 mg in each case) were heated for 7 h at 230 °C in sealed silica tubes. The tubes were filled under argon. Since in the case of copper(II) benzoate with 2-fluoropyridine no reaction occurred at 230 °C, this experiment was repeated at 250 °C. After cooling to ambient temperature, the tubes were opened and the products were analyzed by HPLC. In the case of the halogenated pyridines, the products were also analysed by LC-MS.

Positive-ion ESI-MS data were obtained on an HP1100 quadrupole LC-MS system (Agilent Technologies, Waldbronn, Germany). Mass spectra were obtained in full scan mode from m/z = 50−1000 amu at a fragmentor voltage of 70 V and a capillary voltage of 3000 V. The drying gas flow was 10 L/min and the drying gas temperature was 350 °C.

For reversed-phase HPLC, the black solids produced were dissolved in acetonitrile (2 mL) and then injected into an HP 1090 chromatograph with a Nucleosil 120−5 C18 column (500 × 4 mm) at 50 °C. The products were eluted with a gradient made up of different mixtures of eluents A and B [eluent A: 1 M H_3PO_4 (45 mL), conc. acetic acid (2 mL), and 1 M NaOH (35 mL) were added to water (1500 mL) and the pH of the solution was adjusted to 3.2 with 1 M NaOH; after the addition of acetonitrile (200 mL), the mixture was made up with water to give 2000 mL of eluent A; eluent B: 1 M H_3PO_4 (20 mL), conc. acetic acid (2 mL), and 1 M NaOH (60 mL) were added to water (60 mL) and the pH of the solution was adjusted to 6.6 with 1 M NaOH; after the addition of acetonitrile (1200 mL), the mixture was made up with water to give 2000 mL of eluent B]. A DAD (L-3000 Hitachi) was used for detection at 254 nm.

GC analyses were performed using a Hewlett−Packard series 5890 gas chromatograph, equipped with a 30 m fused silica Megabore column (G. & W. Scientific) with a 5 μm DBI stationary phase. The products were identified with an FID detector; nitrogen was used as the carrier gas. − Elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg. Infrared spectra (KBr pellets) were measured with a Perkin−Elmer 16PC FT-IR instrument.

X-ray Crystallography: Crystallographic data are presented in Table 3; all structural data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication nos. CCDC-152937−152940. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data were collected on a Bruker AXS SMART 1000 diffractometer with a CCD area detector (Mo-K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å) at −100 °C, using the SMART suite of programs.[7] The reflection intensities were integrated using SAINT and corrected for absorption using SADABS.[9,10] The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 with all reflections, using the SHELXTL programs.[11]

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