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Tetranuclear Copper(II) Complexes with Macrocyclic and Open-Chain Disiloxane Ligands as Catalyst Precursors for Hydrocarboxylation and Oxidation of Alkanes and 1-Phenylethanol

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Two new tetranuclear copper(II) complexes $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (**1**) and $[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (**2**), where $\mathbf{H_2L^1}$ is a macrocyclic ligand resulting from [2+2] condensation of 2,6-diformyl-4-methylphenol (DFF) and 1,3-bis(aminopropyl)-tetramethyldisiloxane, and $\mathbf{HL^2}$ is a 1:2 condensation product of DFF with trimethylsilyl *p*-aminobenzoate, have been prepared. The structures of the products were established by X-ray diffraction. The complexes have been characterised by FTIR, UV/Vis spectroscopy, ESI mass-spectrometry and magnetic susceptibility measurements. The latter revealed that the tetranuclear complexes can be described as two ferromagnetically coupled dinuclear units, in which the two copper(II) ions interact antiferromagnetically. The compounds act as homogeneous catalyst precursors for a number of single-pot reactions, including (i) hydrocarboxylation, with CO, H_2O and $K_2S_2O_8$, of a variety of linear and cyclic (n = 5–8) alkanes into the corresponding C_{n+1} carboxylic acids, (ii) peroxidative oxidation of cyclohexane, and (iii) solvent-free microwave-assisted oxidation of 1-phenylethanol.

Introduction

The synthesis of new Schiff base ligands with phenolic groups is an area of active research interest due to their use as models for metal-binding sites in enzymes and because of their capacity to form metal complexes with interesting magnetic exchange interactions, redox and catalytic properties.[1] Schiff bases with azomethine donor groups and bridging phenolic oxygen atoms, referred to as Robson-type ligands,[2] are usually obtained by condensation of an appropriate dialdehyde with a diamine ligand synthon (ligson) in the absence or in the presence of metal ions.[3] The donor groups of these ligands provide clearly distinguished coordination sites that are able to accept two (identical or different) metal ions in close proximity. Recent studies have indicated that the active site in particulate methane monooxygenase (pMMO) is a dicopper centre with a Cu–Cu distance of approximately 2.6 Å,[4] that is capable of oxygen binding;[5] This finding has stimulated interest in dicopper-oxido chemistry[6] in the catalytic oxidation of methane.

2,6-Diformyl-4-methylphenol (DFF) is an appropriate ligson for the synthesis of macrocyclic ligands by reactions with diamines; typically, their isolation is achieved in the form of complexes with metal ions used as templates. Dinuclear complexes with [2+2] macrocycles are the favoured products,[7,8] but [3+3] and [4+4] multinuclear macrocyclic complexes have been reported.[9] Macrocyclic Schiff bases are of particular interest because they can accommodate

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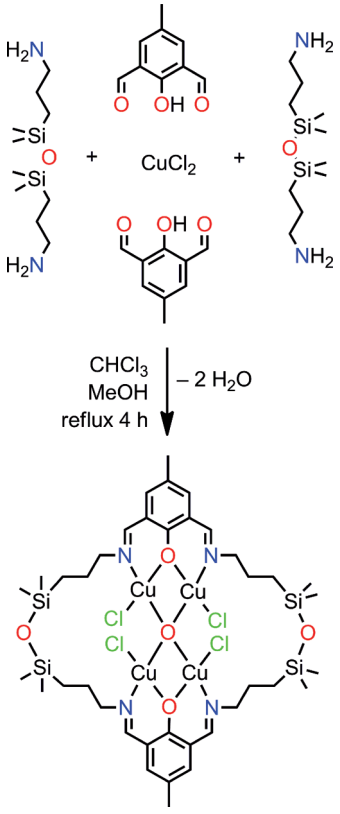
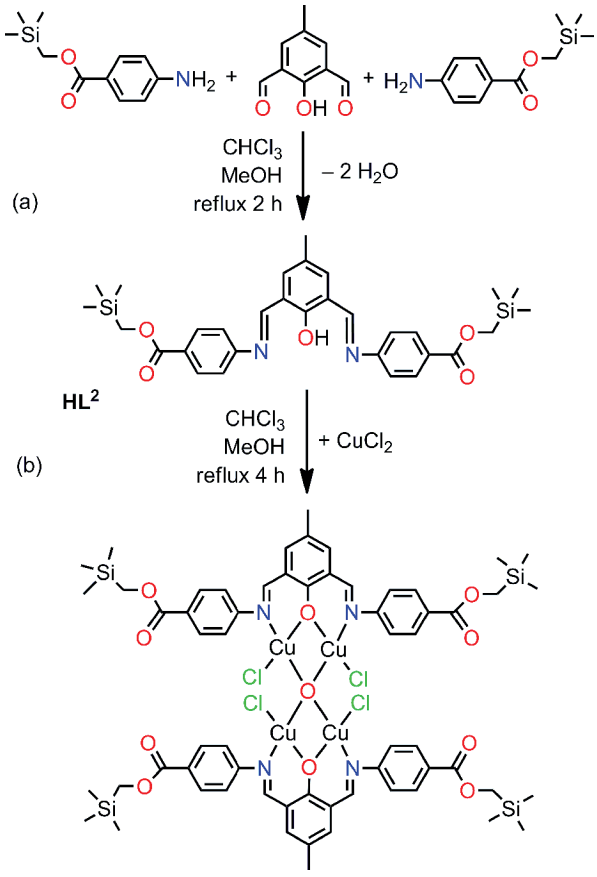
several metal ions, depending on the number, type and position of donor atoms, the ionic radii of metals, and coordination properties of the counterions. Recently, we reported a series of metal complexes with Schiff bases resulting from reactions of disiloxane-containing diamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, with 2-hydroxybenzaldehyde derivatives,[10] pyrrole-2-carbaldehyde[11] or 2,6-diformylphenol.[12] The flexible siloxane unit confers specific properties to the final product, for example, low intermolecular forces, low surface free-energy, large free-volume, good thermal, oxidative and UV stability, and high environmental and bio-compatibility.[13]

Following our interest in metal complexes with both open-chain and macrocyclic siloxane-based ligands, we report herein on the synthesis of two tetranuclear copper(II) complexes, $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (**1**) and $[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (**2**), where $\mathbf{H_2L^1}$ is a macrocyclic ligand resulting from [2+2] condensation of DFF and 1,3-bis(aminopropyl)tetramethyldisiloxane (the only commercially available siloxane-based diamine), and $\mathbf{HL^2}$ is a 1:2 condensation product of DFF with trimethylsilyl *p*-aminobenzoate, which is a new amine prepared in one of our laboratories (see Schemes 1 and 2). The complete characterisation, including single-crystal X-ray diffraction and magnetic susceptibility measurements, are described. Finally, the catalytic activities in hydrocarboxylation and oxidation of alkanes and 1-phenylethanol are reported.



Scheme 1. Synthesis of $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (**1**).



Scheme 2. Synthesis of $[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (**2**).

Results and Discussion

Trimethylsilyl *p*-aminobenzoate was prepared by reaction of *p*-aminobenzoic acid sodium salt with (chloromethyl)trimethylsilane in *N*,*N*-dimethylformamide (DMF) at reflux. Further condensation reaction with 2,6-diformyl-4-methylphenol in 2:1 molar ratio in MeOH/$CHCl_3$ (1:1) afforded the Schiff base, $\mathbf{HL^2}$. The formation of the latter was confirmed by FTIR spectroscopy, which showed the disappearance of the carbonyl and amino absorption bands and the presence of a new band at 1626 cm^{-1}, assigned to the azomethine group. In addition, absorption bands at 1713 cm^{-1} ($C{=}O_{ester}$), 1248 and 853 cm^{-1} ($Si{-}CH_3$), 2955 and 2907 cm^{-1} (C–H from $Si{-}CH_3$ groups) provided further evidence for the identity of $\mathbf{HL^2}$. In the ^1H NMR spectrum, peaks corresponding to C*H*=N proton at δ = 8.83 ppm and those corresponding to the aromatic protons from amine and aldehyde moieties in the region δ = 8.08–7.29 ppm are present, whereas $Si{-}CH_2$ and $Si{-}CH_3$ protons appear at δ = 4.03 and 0.17 ppm, respectively.

The tetranuclear copper(II) complex $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (**1**) was obtained by condensation reaction of 2,6-diformyl-4-methylphenol with 1,3-bis(aminopropyl)tetramethyldisiloxane followed by addition of $CuCl_2{\cdot}2H_2O$ in methanol in 1:1:2 molar ratio, as shown in Scheme 1. Slow evaporation of the reaction mixture generated green crystals that were of suitable quality for X-ray diffraction in 18% yield.

The copper complex $[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (**2**) was obtained by the reaction of $\mathbf{HL^2}$ with copper(II) chloride in 1:2 molar ratio in MeOH/$CHCl_3$ (1:1), in the presence of triethylamine as base (Scheme 2). After slow evaporation of the solvent mixture at room temperature, the crude product was purified by column chromatography (dichloromethane/methanol, 99:1).

A strong absorption band at 1634 cm^{-1} in the FTIR spectrum of **1** is presumably due to azomethine group vibration.[14,15] The OH stretching vibration of 2,6-diformyl-4-methyphenol is not seen in the spectrum of the complex, indicating its deprotonation and coordination to copper(II). A series of bands assigned to the C_{Ar}–O stretching vibrations of the coordinated phenolato group[16] is observed from 1000 to 1150 cm^{-1}. These were partially overlapped with absorptions assigned to the Si–O–Si bonds from siloxane groups.[17] The bands observed in the 420–492 cm^{-1} region might be due to the ν(Cu–N) and ν(Cu–O) vibrations.[18] UV/Vis absorption spectrum of **1** shows two bands, one intense absorption at 375 nm (ε = 19180 $M^{-1}cm^{-1}$) and a weak band with a maximum at 655 nm (ε = 236 $M^{-1}cm^{-1}$), whereas that of **2** exhibited three absorptions with maxima at 384 (ε = 38300 $M^{-1}cm^{-1}$), 415 (ε = 38060 $M^{-1}cm^{-1}$) and 745 (ε = 550 $M^{-1}cm^{-1}$) nm. The appearance of the intense bands is due to a combination of π-π* transition of the azomethine chromophore and ligand-to-metal charge transfer (LMCT) transition,[19–23] whereas those at 655 and 745 nm for **1** and **2** respectively are due to d-d transitions. The LMCT band(s) presumably arise from electron transfer from the π-orbital of the phenolato ligand to the empty d-orbital of the Cu^{II} ion.[23,25] A strong peak at *m*/*z* 1127 in the positive ion ESI mass spectrum of **1** was attributed to $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]^+$.

Other spectral properties and the elemental analysis of compound **2** are in good agreement with the formulation of the complex $[Cu_4\ (\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ established by X-ray crystallography. A weak signal at *m*/*z* 1561 in positive ion ESI mass spectrum was assigned to $[M + H]^+$, whereas that of medium intensity at *m*/*z* 637 was assigned to $[Cu(\mathbf{HL^2})]^{2+}$.

X-ray Crystallography

The results of X-ray diffraction studies of **1** and **2** are shown in Figures 1 and 2 (see also S1 in the Supporting Information), along with selected bond lengths and bond angles quoted in the captions to figures. Compounds **1** and **2** crystallise in the triclinic $P\bar{1}$, and orthorhombic *Pbca* space groups, respectively, and no co-crystallised solvent was found in either crystals. The central part of molecules of **1** and **2** consists of a tetranuclear $\{Cu_4\}$ core held together by a μ_4-oxido ligand. One doubly-deprotonated macrocyclic ligand $(\mathbf{L^1})^{2-}$ in **1**, and two mono-deprotonated ligands $(\mathbf{L^2})^-$ in **2** are coordinated to the four copper(II) ions through four nitrogen atoms and two phenolato oxygen donors. In fact, they behave as bidentate chelating ligands for each of the four Cu^{II} ions. The slightly distorted square-planar geometry of each metal centre is completed by a chloride anion and the central μ_4-oxido ligand. In both **1** and **2**, the four copper ions of the $\{Cu_4(\mu_4\text{-}O)\}$ core are located at the vertices of a distorted tetrahedron around the central μ_4-oxido ligand with ∠Cu1–O1–Cu2 102.9(2)°, ∠Cu3–O1–Cu4 103.2(2)° and ∠Cu1–O1–Cu4 98.7(2)°, ∠Cu2–O1–Cu3 101.7(2)° for **1** and 103.4(4)°, 103.1(4)°, 106.8(4)° and 114.9(5)° for **2**, respectively. The two phen-

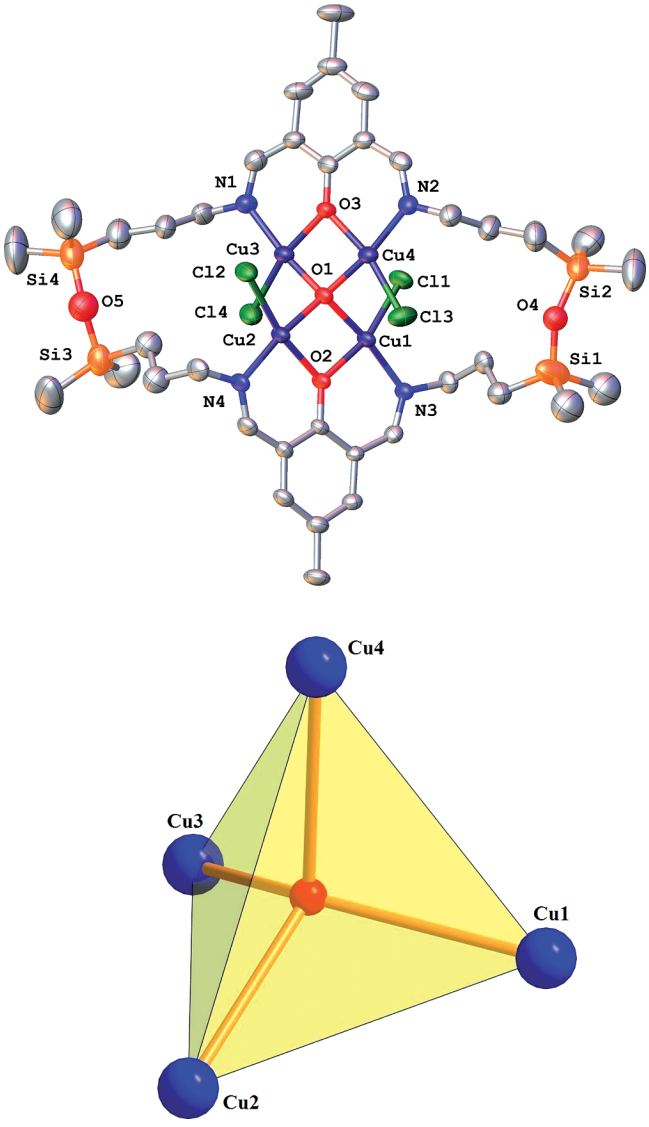


Figure 1. (top) ORTEP view of $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (**1**); (bottom) the tetrahedral $\{Cu_4(\mu_4\text{-}O)\}$ core. Selected bond lengths [Å] and bond angles [°]: Cu1–Cl1 2.257(2), Cu1–O1 1.923(4), Cu1–O2 1.967(3), Cu1–N3 1.957(4), Cu2–Cl2 2.249(2), Cu2–O1 1.912(4), Cu2–O2 1.965(3), Cu2–N4 1.959(4), Cu3–Cl3 2.248(2), Cu3–O1 1.903(4), Cu3–N1 1.964(5), Cu3–O3 1.977(4), Cu4–Cl4 2.241(2), Cu4–O1 1.926(4), Cu4–N2 1.967(5), Cu4–O3 1.977(4), O1–Cu1–Cl1 88.6(1), O1–Cu1–O2 78.7(2), O1–Cu1–N3 170.3(2), O2–Cu1–Cl1 164.7(1), N3–Cu1–Cl1 101.1(1), N3–Cu1–O2 91.8(2), O1–Cu2–Cl2 89.6(1), O1–Cu2–O2 79.0(2), O1–Cu2–N4 171.1(2), O2–Cu2–Cl2 168.1(1), N4–Cu2–Cl2 99.1(2), N4–Cu2–O2 92.3(2), O1–Cu3–Cl3 90.5(1), O1–Cu3–N1 169.8(2), O1–Cu3–O3 79.3(2), N1–Cu3–Cl3 99.2(2), N1–Cu3–O3 91.5(2), O3–Cu3–Cl3 167.0(1), O1–Cu4–Cl4 89.3(1), O1–Cu4–N2 170.1(2), O1–Cu4–O3 78.7(2), N2–Cu4–Cl4 100.5(2), N2–Cu4–O3 91.5(2), O3–Cu4–Cl4 167.4(1).

olato-bridged copper pairs in **1** are not exactly perpendicular, with a dihedral angle between the two Cu_2O_2 planes of 70.00(3)°, whereas in compound **2** this angle is 93.05(8)°. This difference correlates well with the Cu···Cu separations along the edges of the {$Cu_4(\mu_4$-O)} tetrahedron. Two of them in **1**, supported by the phenolato-bridge, show close Cu1···Cu2 and Cu3···Cu4 distances of 2.9985(9) and 3.001(1) Å, respectively. The four other edges, which have no additional support apart from the central O1 atom, vary in a quite wide range from Cu1···Cu4 at 2.9213(4) Å, Cu2···Cu3 at 2.958(1) Å to Cu1···Cu3 at 3.418(1) Å and Cu2···Cu4 at 3.4284(9) Å. Accordingly, in **1**, the {$Cu_4(\mu_4$-O)} tetrahedron is heavily distorted. In contrast, in the case of **2**, the tetrahedron is much more regular, with Cu···Cu distances varying by less than 0.25 Å compared with 0.5 Å in **1**. The constraints imposed by the macrocyclic ligand $(\mathbf{L^1})^{2-}$ upon coordination to the four copper atoms, which is shown in Figure S2, are the main reason for the distortion of the {$Cu_4(\mu_4$-O)} tetrahedron in **1** compared with that in **2**. In this respect, it is worth noting that in the previously reported tetranuclear complexes,[24] the {Cu_4O} core is almost regular.

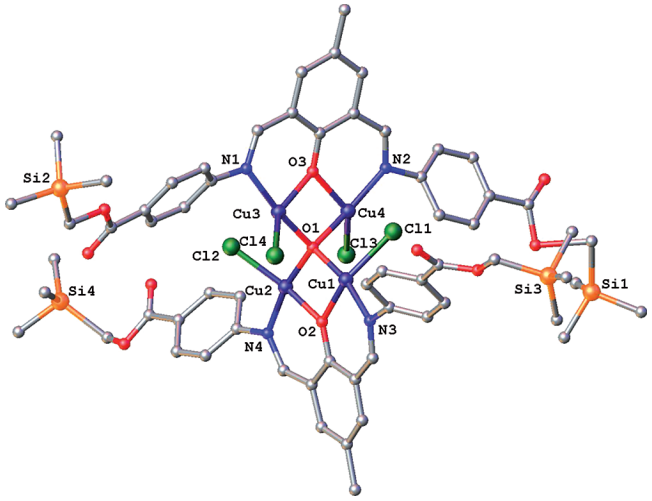


Figure 2. X-ray diffraction structure of [$Cu_4(\mu_4$-O)($\mathbf{L^2}$)$_2$Cl$_4$] (**2**). Selected bond lengths [Å] and bond angles [°]: Cu1–Cl1 2.231(5), Cu1–O1 1.911(9), Cu1–O2 1.958(9), Cu1–N3 1.95(1), Cu2–Cl2 2.226(4), Cu2–O1 1.904(9), Cu2–O2 1.990(9), Cu2–N4 1.97(1), Cu3–Cl3 2.257(4), Cu3–O1 1.886(8), Cu3–N1 1.95(1), Cu3–O3 1.99(1), Cu4–Cl4 2.291(4), Cu4–O1 1.925(9), Cu4–N2 1.96(1), Cu4–O3 1.987(9), O1–Cu1–Cl1 92.2(3), O1–Cu1–O2 79.2(4), O1–Cu1–N3 167.5(5), O2–Cu1–Cl1 144.5(3), N3–Cu1–Cl1 100.2(4), N3–Cu1–O2 91.0(4), O1–Cu2–Cl2 89.1(3), O1–Cu2–O2 78.6(4), O1–Cu2–N4 168.3(5), O2–Cu2–Cl2 147.0(3), N4–Cu2–Cl2 102.6(4), N4–Cu2–O2 91.5(4), O1–Cu3–Cl3 91.5(3), O1–Cu3–N1 170.6(5), O1–Cu3–O3 80.2(4), N1–Cu3–Cl3 97.4(4), N1–Cu3–O3 90.8(4), O3–Cu3–Cl3 145.7(3), O1–Cu4–Cl4 88.7(3), O1–Cu4–N2 165.1(4), O1–Cu4–O3 79.5(4), N2–Cu4–Cl4 105.8(3), N2–Cu4–O3 91.2(4), O3–Cu4–Cl4 139.8(3).

Magnetic Properties

The results of magnetic susceptibility measurements on the polycrystalline tetranuclear clusters **1** and **2** are depicted in Figure 3. At room temperature, the χ_MT products for **1** and **2** are 0.338 and 0.366 cm^3 K mol^{-1}, respectively. These values are much lower than the value (1.5 cm^3 K mol^{-1}) expected for four uncoupled Cu^{II} ions (S = 1/2, g = 2). Upon decreasing the temperature, the χ_MT product sharply decreases to reach 0.003 cm^3 K mol^{-1} for **1** and 0.004 K mol^{-1} for **2** at 100 K. Below 100 K the χ_MT product remains close to zero for both compounds (Figure 3). The overall shape of the curve indicates dominant antiferromagnetic interactions within the tetranuclear complex, leading to S = 0 ground state, which is the only populated state below 100 K. To quantify this behaviour, the magnetic susceptibility data of clusters **1** and **2** were analysed by using the general spin-Hamiltonian describing the isotropic exchange interactions in Cu_4 clusters, see Equation (1).[25–29]

$$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_1S_3 - 2J_3(S_2S_3 + S_1S_4) - 2J_4S_2S_4 \quad (1)$$

J_1, J_2, J_3 and J_4 are exchange parameters sketched in Figure 3 and S_i is the spin operator for the individual Cu^{II} ions. The eigenfunctions of this spin-Hamiltonian[32–36] Equation (1) are given in the Supporting Information (Figure S2). The Van Vleck equation then gives the expression for the molar susceptibility as Equation (2).

$$\chi_M = \frac{N_A g_{Cu}^2 \beta}{k_B T} \cdot \frac{10e^{-\frac{E_1}{k_B T}} + 2e^{-\frac{E_2}{k_B T}} + 2e^{-\frac{E_3}{k_B T}} + 2e^{-\frac{E_4}{k_B T}}}{5e^{-\frac{E_1}{k_B T}} + 3e^{-\frac{E_2}{k_B T}} + 3e^{-\frac{E_3}{k_B T}} + 3e^{-\frac{E_4}{k_B T}} + e^{-\frac{E_5}{k_B T}} + e^{-\frac{E_6}{k_B T}}} \quad (2)$$

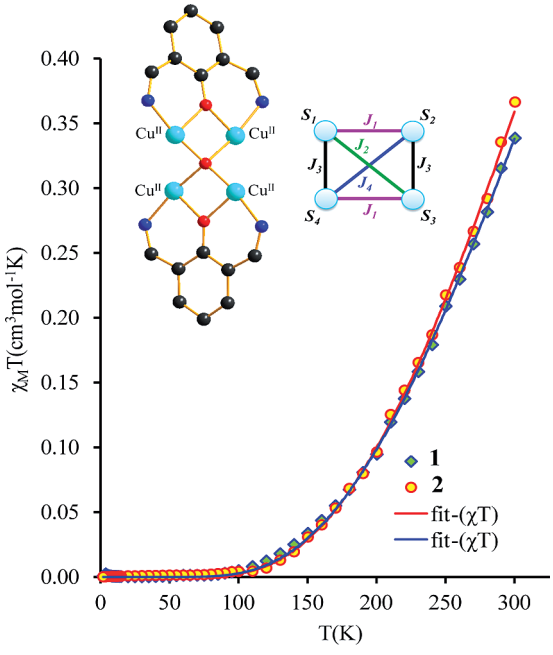


Figure 3. Plot of χ_MT vs. T for **1** and **2**. The solid lines correspond to the best fits obtained by using Equation (2) with parameters indicated in the text.

Fits of the experimental data by using Equation (2) yielded the following sets of parameters for compound **1**: J_1 = –277(3) cm^{-1}, J_2 = +15(2) cm^{-1}, J_3 = +75(6) cm^{-1}, J_4

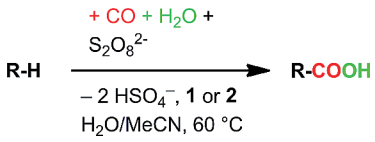
= +15(2) cm^{-1}, g = 2.08(2), $R = 3.2 \times 10^{-4}$, and for **2**: J_1 = –296(4) cm^{-1}, J_2 = +20(3) cm^{-1}, J_3 = +95(7) cm^{-1}, J_4 = +20(3) cm^{-1}, g = 2.28(2), $R = 5.9 \times 10^{-4}$. The dominant interaction J_1 is antiferromagnetic; it couples the two pairs of phenolato-bridged copper(II) ions. These two pairs of metal ions are then coupled ferromagnetically (J_2, J_3, J_4) through the central oxido ligand.

The determination of the energy levels for **1** and **2** confirms that the ground state is a singlet ($E_{S=0}{}^6$ = –824.8 cm^{-1} for **1** and –881.76 cm^{-1} for **2**). At room temperature, the paramagnetism of **1** and **2** is essentially due to the population of the spin state S = 1 located approximately 500 cm^{-1} above the ground state.

To understand these results, it is necessary to perform an orbital analysis and undertake magneto-structural correlations. For the four copper(II) ions, the so-called magnetic orbital resides in the N_2OCl plane. The magnetic orbitals of Cu1 and Cu2 are coplanar. This also holds for the magnetic orbitals of Cu3 and Cu4. Moreover, the angles of the oxido and phenoxido bridges between these atoms are well above 100°. Accordingly, there is a strong overlap between the magnetic orbitals and, hence, following Kahn's model,[30,31] a strong antiferromagnetic interaction (J_1) is expected. This is what is observed here, in agreement with previous experimental reports.[38,32,33,34,35] In contrast, the dihedral angle between the basal planes of Cu1 and Cu4 is 70° for **1** and 93° for **2**. The overlap between the magnetic orbitals is then markedly reduced. Moreover, the angles Cu–O1–Cu in **1** and **2** are in the range of 98.7–114.9°. Accordingly, J_3 is strongly ferromagnetic. Finally, the structural situation driving the values of J_2 and J_4 is intermediate, leading to a moderate ferromagnetic interaction. The marked differences between N–Cu–Cl and O–Cu–Cl angles do not have an appreciable impact on the J values because of the absence of bridges along these directions. However, they probably have an impact on increasing the g value [g = 2.08(2) (**1**) and g = 2.28(2) (**2**)], which is larger in the case of the more distorted copper polyhedron of **2**.

Hydrocarboxylation of Linear and Cyclic Alkanes

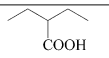
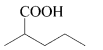
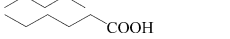
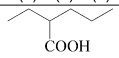
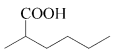
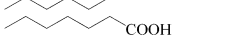
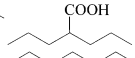
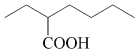
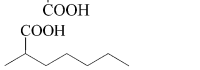
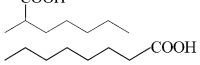
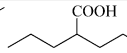
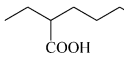
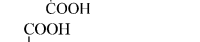
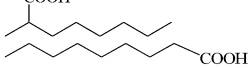
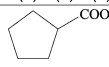
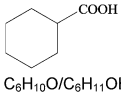
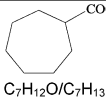
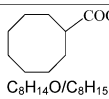
The studies were performed according to a previously developed method,[36] which involves the reaction of a C_n alkane with carbon monoxide (carbonyl source) and water (hydroxy source) in the presence of peroxodisulfate $S_2O_8^{2-}$ and the catalyst precursor at 50–60 °C in water/acetonitrile medium, to form a C_{n+1} carboxylic acid (Scheme 3).



Scheme 3. Mild, one-pot hydrocarboxylation of C_n (n = 5–8) alkanes to give C_{n+1} carboxylic acids.

Both complexes **1** and **2** act as efficient catalyst precursors towards the hydrocarboxylation of C_5–C_8 linear (*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) and cyclic (cyclopentane, cyclohexane, cycloheptane and cyclooctane)

Table 1. Substrate versatility and selectivity in the direct hydrocarboxylation of linear and cyclic C_n alkanes to C_{n+1} carboxylic acids catalysed by **1** and **2**.[a]

Entry	Alkane C_n	C_{n+1} carboxylic acid (yield, %)[b]	Complex **1**	Complex **2**
1	*n*-C_5H_{12}		7.5	5.4
			15.2	10.8
			0.7	0.8
		total	23.4	17.0
		C(1):C(2):C(3)[c]	1:32:32	1:20:20
2	*n*-C_6H_{14}		12.5	8.2
			13.0	8.8
			0.8	0.8
		total	26.3	17.8
		C(1):C(2):C(3)[c]	1:24:23	1:17:15
3	*n*-C_7H_{16}		3.7	3.5
			9.3	7.1
			8.8	7.2
			0.6	0.7
		total	22.4	18.5
		C(1):C(2):C(3):C(4)[c]	1:22:23:19	1:15:15:15
4	*n*-C_8H_{18}		5.0	3.6
			5.1	3.8
			5.5	4.2
			0.4	0.4
		total	16.0	12.0
		C(1):C(2):C(3):C(4)[c]	1:27:25:25	1:16:14:13
5			22.1	17.0
		C_5H_8O/C_5H_9OH[d]	2.6/0.4	1.8/0.8
		total	25.1	19.6
6[e]			34.2	24.1
		$C_6H_{10}O/C_6H_{11}OH$[d]	1.7/0.6	0.8/0.6
		total	36.4	25.5
7			18.3	17.5
		$C_7H_{12}O/C_7H_{13}OH$[d]	5.0/2.4	4.6/2.6
		total	25.7	24.7
8			14.4	9.7
		$C_8H_{14}O/C_8H_{15}OH$[d]	10.8/1.6	4.4/4.2
		total	26.8	18.3

[a] Reaction conditions (unless stated otherwise): alkane (1.00 mmol), p(CO) = 20 atm (5.32 mmol), $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL)/MeCN (4.0 mL), complex **1** or **2** (4.0 μmol), 60 °C, 4 h in a stainless steel autoclave (13.0 mL capacity). [b] Yield (%) (mols of carboxylic acid/100 mol of alkane) determined by GC analysis. [c] Selectivity parameter C(1)/C(2)/C(3)/C(4) indicates the regioselectivity, meaning the normalised (for the relative number of hydrogen atoms) reactivities of H atoms at different positions of linear alkane chains. [d] Ketone and alcohol are formed as a result of alkane oxidation. [e] H_2O (3.0 mL)/MeCN (3.0 mL), 50 °C.

alkanes into C_6–C_9 carboxylic acids with overall yields up to 36% based on the alkane (Table 1). Such activity is considerable taking into account the high degree of inertness of alkanes and the very mild reaction conditions. Linear alkanes containing both secondary (more reactive) and primary carbon atoms are carboxylated into a mixture of isomeric acids. However, the branched acids are formed as the main products, with the yields of the linear acids being negligible (0.4–0.8%). The highest yield was observed in the presence of **1** for the *n*-hexane hydrocarboxylation (26%), followed by *n*-pentane (23%), *n*-heptane (22%) and *n*-octane (16%), whereas in the presence of **2** those yields were in the range of 12–18%.

Hydrocarboxylation of the cyclic alkanes catalysed by **1** and **2** results in the formation of only one carboxylic acid product due to the existence of a single type of carbon atom in their molecules. The highest activity was observed in the case of **1** for cyclohexane, leading to 34% yield of $C_6H_{11}COOH$, followed by cyclopentane (22% of C_5H_9COOH). The yield of carboxylic acids drops to 18 and 14% for cycloheptane and cyclooctane, respectively. The corresponding cyclic ketone and alcohol were also detected products, being formed from partial alkane oxidation. The total yield of oxygenates (ketone is formed in preference to alcohol) increases with the hydrocarbon size, namely from 2% for C_6H_{12} to 12% for C_8H_{16}.

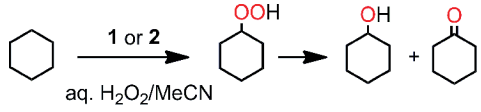
The hydrocarboxylation of C_6H_{12} promoted by **2** leads to a carboxylic acid yield of approximately 24%, followed by 17% for C_5H_{10} and C_7H_{14}, and 10% for C_8H_{16}.

Based on the previous background[36] and on the selectivity parameters[37] observed herein [see C(1)/C(2)/C(3)/C(4) ratio; Table 1] a free-radical mechanism for the alkane hydrocarboxylation can be proposed. The alkyl radicals R$^{\cdot}$ are formed by hydrogen abstraction from the alkanes by $SO_4^{\cdot-}$ (sulfate radical derived from thermolysis of $K_2S_2O_8$). Then R$^{\cdot}$ reacts very rapidly with CO, forming the acyl radical RCO$^{\cdot}$, which is further oxidised by active Cu^{II} species (or by $K_2S_2O_8$) to the acyl cation RCO^+. This is finally hydrolysed by water to form the carboxylic acid RCOOH.

The yields achieved herein in alkane hydrocarboxylation are comparable to those obtained earlier in the presence of other multicopper(II) derivatives bearing amino alcoholate ligands.[36e]

Peroxidative Oxidation of Cyclohexane

Copper compounds **1** and **2** were tested as catalyst precursors in the oxidation of cyclohexane by H_2O_2 (50% aqueous solution) at 50 °C in MeCN/H_2O medium (Scheme 4). The reaction was monitored by gas chromatography to determine the amount of cyclohexanol and cyclohexanone formed, typically after treatment with PPh_3 (to reduce cyclohexyl hydroperoxide to cyclohexanol).[38]



Scheme 4. Oxidation of cyclohexane to cyclohexanol and cyclohexanone.

The accumulation of oxygenated products (cyclohexanol and cyclohexanone) in the cyclohexane oxidation catalysed by **1** and **2**, in the absence or in the presence of trifluoroacetic acid (TFA) are given in Table 2 and Figure 4. Both complexes catalyse this reaction in the absence of any added acid with approximately 8% of total product yield reached after ca. 30 min (entries 3 and 15, for **1** and **2**, respectively). Further increase of the reaction time did not affect the total yield of the products. However, the presence of TFA improved the catalytic performance of both copper compounds, and the total yield of cyclohexanol and cyclohexanone achieved a maximum value of approximately 14% after 1 h (entry 11). Other acids were tested, for example, HNO_3 and pyrazinecarboxylic acid (PCA), but with a much lower effect on the yield. The promoting effect of an acid cocatalyst is well known for other Cu-catalysed systems in the oxidative transformation of alkanes.[39] The activity exhibited by compounds **1** and **2**, in the absence of TFA, is higher than that shown, for example, by $[Cu(OTf)_2(Py_2S_2)]$ {Py_2S_2 = 1,6-bis(2′-pyridyl)-2,5-dithiahexane} (with 4.3% overall yield)[40] and comparable to those of the complexes bearing azathia macrocycles such as $[Cu(OTf)_2(\mathbf{L^3})]$ ($\mathbf{L^3}$ = mixed 14-membered N_2S_2 azathia macrocycle) or [Cu-

Table 2. Total yield (cyclohexanol and cyclohexanone) versus time in the oxidation of cyclohexane by H_2O_2 (50% aqueous solution) at 50 °C in CH_3CN catalysed by **1** or **2**.[a]

Entry	Precat.	Acid cocat.	Time [min]	Yield [%][b] OL	ONE	Total	TON[c]
1	**1**	–	5	3.8	3.3	7.1	65
2	**1**	–	15	3.6	4.0	7.6	70
3	**1**	–	30	3.2	4.8	8.0	72
4	**1**	–	45	3.3	4.7	8.0	73
5	**1**	–	60	3.8	4.2	8.0	74
6	**1**	–	120	4.2	4.6	8.8	80
7	**1**	TFA	5	2.0	2.4	4.4	41
8	**1**	TFA	15	4.4	2.8	7.2	67
9	**1**	TFA	30	5.4	4.6	10.0	92
10	**1**	TFA	45	6.2	6.0	12.2	112
11	**1**	TFA	60	7.0	7.0	14.0	129
12	**1**	TFA	120	6.8	5.9	12.7	117
13	**2**	–	5	4.1	3.0	7.1	65
14	**2**	–	15	4.6	2.7	7.3	68
15	**2**	–	30	4.6	2.9	7.5	69
16	**2**	–	45	5.3	2.3	7.6	70
17	**2**	–	60	5.0	2.6	7.6	70
18	**2**	–	120	5.5	2.5	8.0	74
18	**2**	TFA	5	2.4	1.9	4.3	39
20	**2**	TFA	15	3.7	2.8	6.4	59
21	**2**	TFA	30	5.9	3.4	9.3	85
22	**2**	TFA	45	7.4	4.6	12.0	111
23	**2**	TFA	60	8.4	4.8	13.2	122
24	**2**	TFA	120	7.9	4.4	12.3	113

[a] Reaction conditions: cyclohexane (0.46 M), catalyst precursor **1** or **2** (5×10^{-4} M), TFA (5×10^{-3} M), H_2O_2 (50% aq, 2.2 M), MeCN (up to 5 mL total volume), 50 °C. [b] Moles of products [cyclohexanol (OL) + cyclohexanone (ONE)]/100 mol of cyclohexane, determined by GC analysis after treatment with PPh_3. [c] Moles of products (cyclohexanol + cyclohexanone) per mol of catalyst precursor.

(OTf)($\mathbf{L^4}$)(H_2O)](OTf) ($\mathbf{L^4}$ = nine-membered NS_2 macrocyclic ligand with a pendant 2-methylpyridyl arm) (overall yield ca. 8%).[41] However, for these triflate complexes, and in contrast to **1** and **2**, no considerable acid-promoting effect was observed (in the case of the latter triflate complex, acid even had an inhibiting effect[41]).

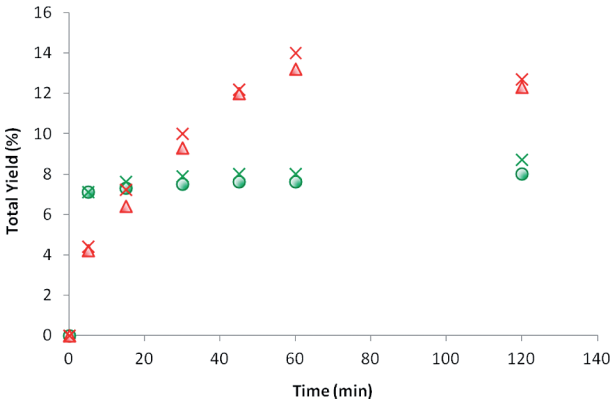
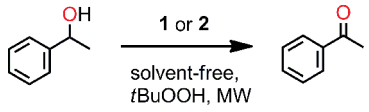


Figure 4. Total yield (cyclohexanol and cyclohexanone) versus time in the oxidation of cyclohexane by H_2O_2 (50% aqueous solution) catalysed by **1** in the absence of any additive (green cross) or in the presence of TFA (1:10) (red cross), or by **2** in the absence of any additive (green circles) or in the presence of TFA (1:10) (red triangles), at 50 °C in CH_3CN.

Despite the lower promoting effect of the acid observed for **1** and **2**, relative to a copper(II) dimer with 3-(2-hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione [overall yield ca. 27% for $n(HNO_3)/n$(Cat) = 10 and $n(C_6H_{12})/n$(Cat) = 50][42] or mononuclear triethanolamine complex [Cu(H_2tea)(N_3)],[43] for which no more than 2% conversion was achieved, good performance of the new catalysts **1** and **2** was achieved in the absence of any acid.

Solvent-Free Microwave-Assisted Oxidation of 1-Phenylethanol

The investigation of the catalytic properties of copper(II) complexes **1** and **2** towards the oxidation of 1-phenylethanol as model substrate was undertaken by following our previously developed procedure[12,44] (Scheme 5), under mild conditions using *tert*-butyl hydroperoxide (*t*BuOOH, aq. 70%, 2 equiv.) as oxidising agent, under typical conditions of 80 °C, low power (5 W) microwave (MW) irradiation, 3 h reaction time and in the absence of any added solvent.



Scheme 5. MW-assisted solvent-free oxidation of 1-phenylethanol to acetophenone.

The acetophenone was the only oxidation product obtained from these MW-assisted transformations, and the high selectivity observed (typically > 98%) was confirmed by mass balances; the results are summarised in Table 3.

Table 3. MW-assisted, solvent-free oxidation of 1-phenylethanol to acetophenone by **1** and **2**.[a]

Entry	Catalyst precursor	Time [h]	Additive [μmol]	Yield [%][b]	TON[c]	TOF [h^{-1}][c]
1	1	3	–	62	827	276
2	1	3	Ph_2NH (100)	3	14	5
3	1	3	TEMPO (30)	11	87	29
4[d]	1	0.5	–	74	368	735
5[d]	1	0.5	TFA (25)	89	511	1.0×10^3
6[d]	1	0.5	TFA (50)	76	399	798
7[d]	1	0.5	Hpca (50)	33	169	338
8[d]	1	0.5	HNO_3 (50)	21	101	202
9	2	3	–	82	826	276
10[e]	2	3	–	65	1.1×10^3	361
11	2	0.5	Ph_2NH (100)	4	21	7
12[d]	2	0.5	–	76	367	734
13[d]	2	0.5	TFA (25)	78	344	688
14	2	0.5	TEMPO (30)	6	29	58

[a] Reaction conditions (unless stated otherwise): substrate (2.5 mmol), catalyst precursor **1** or **2** (5 μmol; 0.2 mol-% vs. substrate), *t*BuOOH (aq. 70%, 5 mmol), 80 °C, microwave irradiation (5 W). [b] Molar yield (%) based on substrate; i.e., moles of product per 100 mol of substrate determined by GC analysis. [c] Turnover number = number of moles of product per mol of metal catalyst; TOF = TON per hour. [d] Reaction performed at 120 °C (20 W). [e] Catalyst **2** (1.5 μmol, 0.06 mol-% vs. substrate).

Complexes **1** and **2** catalyse efficiently this reaction and, under such conditions, the reactions led to 62 and 82% acetophenone, respectively (Table 3, entries 1 and 9), for a catalyst/substrate molar ratio of 0.2%. The yield was comparable with those obtained previously in the solvent-free oxidation of 1-phenylethanol catalysed by copper(II) complexes containing tetradentate N_2O_2 ligands[45] or copper(II) Schiff base complexes with *O*,*N*,*O*-donors.[46]

The temperature had an accelerating effect and an increase from 80 (5 W) to 120 °C (20 W) allowed yields of ca. 75% acetophenone to be achieved in only 30 min (Table 3, entries 4 and 12).

The effect of the amount of catalyst precursor **2** was also studied. Its decrease, at 80 °C, from 5 to 1.5 μmol [*n*(catalyst **2**)/*n*(substrate) from 0.2 to 0.06%] (Table 3, entries 9 and 10) resulted in a reduction in yield from 82 to 65%, but TON (moles of product/mol of catalyst) increased from 826 to 1100.

The addition of trifluoroacetic acid (TFA) had a beneficial effect on both catalytic systems, resulting into a maximum yield of 89% and a TON of 511 (Table 3, entry 5), in the presence of **1** (at 120 °C/20 W) for the relatively low amount of 25 μmol TFA [*n*(acid)/*n*(catalyst **1**) = 5]. The addition of the heteroaromatic 2-pyrazinecarboxylic acid (Hpca) or of nitric acid (HNO_3) has the opposite effect; i.e., a drop in the yield was observed in the presence of 50 μmol [*n*(acid)/*n*(catalyst **1**) = 10] of either of these acids (Table 3, entries 7 and 8).

The effect of the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical that is a known[47–51] promoter in aerobic oxidation of alcohols, was also evaluated; however, an inhibiting effect was observed (Table 3, entries 3 and 14, for **1** and **2**, respectively).

The addition of Ph_2NH, a known O-centred radical trap,[52] almost completely suppressed the catalytic activity, thus suggesting[41,45,46,53] the involvement of a radical mechanism. The mechanism may involve the metal-assisted generation of *t*BuOO· and *t*BuO· radicals (upon oxidation and reduction of *t*BuOOH by a Cu^{II} or a Cu^{I} centre, respectively),[54,55] with the latter behaving as an H-atom abstractor from the alcohol.[54–57]

Conclusions

Two new Schiff base copper(II) complexes derived from DFF and 1,3-bis(aminopropyl)tetramethyldisiloxane, and DFF and trimethylsilyl *p*-aminobenzoate, $[Cu_4(\mu_4\text{-}O)(\mu_2\text{-}\mathbf{L^1})Cl_4]$ (**1**) and $[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (**2**), were prepared. The complexes were characterised by elemental analysis, spectroscopic methods (IR, UV/Vis), positive ion ESI mass spectrometry, and single-crystal X-ray diffraction. The magnetic measurements revealed that the ground state of **1** and **2** is a singlet, whereas, in agreement with the magnetostructural analysis, the fit of the magnetic susceptibility in the whole temperature range reveals that **1** and **2** can be regarded as a ferromagnetically-coupled set of antiferromagnetically-coupled (J_1) dinuclear units. The obtained compounds act as catalyst precursors for hydrocarboxylation of a variety of C_5–C_8 linear (*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) and cyclic (cyclopentane, cyclohexane, cycloheptane and cyclooctane) alkanes to give C_6–C_9 carboxylic acids with overall yields up to 36% based on the alkane. The linear alkanes are carboxylated to give a mixture of isomeric acids, with predominance of those formed upon carboxylation of secondary C atoms, in comparison with the primary C atoms. Complex **1** showed a slightly higher activity in comparison with **2**. For both linear and cyclic alkanes, the highest yields were observed for the hydrocarboxylation of the corresponding C_6 alkanes (*n*-hexane and cyclohexane, respectively), being followed by the C_5 alkanes. This work also shows that compounds **1** and **2** act as catalyst precursors for the peroxidative oxidations of cyclohexane (with H_2O_2) to give cyclohexanol and cyclohexanone, and of 1-phenylethanol to give acetophenone (with *t*BuOOH), with the latter being conducted under solvent-free microwave irradiation conditions. The reactions are believed to occur through radical mechanisms. Overall, this study opens up the application of copper complexes with siloxane-based ligands to the above types of oxidation catalysis, and such processes merit further exploration.

Experimental Section

Materials: 2,6-Diformyl-4-methylphenol (Polivalent-95), 1,3-bis(aminopropyl)tetramethyldisiloxane (Alfa Aesar), copper(II) chloride dihydrate (Aldrich), (chloromethyl)trimethylsilane (Aldrich), *p*-aminobenzoic acid (Aldrich), triethylamine (Aldrich), sodium hydroxide (Aldrich), methanol (Chimopar), dichloromethane (Chimopar), chloroform (Chimopar), dimethylformamide (Aldrich), diethyl ether (Aldrich), were used as received from commercial suppliers. Trimethylsilyl *p*-aminobenzoate was prepared by the reaction of *p*-aminobenzoic acid sodium salt with (chloromethyl)trimethylsilane in dimethylformamide at reflux. The identity of the synthesised amine was confirmed by spectroscopic methods: FTIR (KBr pellet): $\tilde{\nu}$ = 3414, 3346, 3229 (NH_2), 1692 ($C{=}O_{ester}$), 1250 and 849 ($Si–CH_3$) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, J = 8.4 Hz, 2 H, Ar-*H*), 6.64 (d, J = 8.4 Hz, 2 H, Ar-*H*), 4.03 (s, 2 H, NH_2), 3.94 (s, 2 H, CH_2), 0.13 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 167.44, 150.59, 131.47, 120.33, 113.80, 57.41, –2.95 ppm.

Preparation of Complexes and Ligands

$[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_4]$ (1): To a solution of 1,3-bis(aminopropyl)-tetramethyldisiloxane (0.33 g, 1.33 mmol) in methanol (10 mL) was added dropwise a solution of 2,6-diformyl-4-methylphenol (0.22 g, 1.33 mmol) in methanol (10 mL) and the reaction mixture was stirred and heated to reflux for 2 h. A solution of $CuCl_2{\cdot}2H_2O$ (0.45 g, 2.66 mmol) in methanol (20 mL) was added and heating was continued for 4 h. Finally, the reaction mixture was filtered and the solution was allowed to stand at room temperature. Dark-green crystals of X-ray diffraction quality were filtered off after five days, washed with methanol (2× 3 mL) and dried in air, yield 0.29 g (18.3%). FTIR (KBr pellet): $\tilde{\nu}$ = 3549 (w), 3416 (m), 2951 (m), 2918 (m), 2899 (m), 2868 (m), 1634 (vs), 1618 (s), 1562 (vs), 1458 (s), 1410 (m), 1385 (m), 1342 (s), 1306 (w), 1288 (w), 1254 (s), 1186 (m), 1051 (s), 991 (m), 968 (w), 874 (w), 835 (vs), 797 (s), 777 (s), 768 (s), 741 (w), 702 (w), 619 (m), 571 (w), 532 (vw), 509 (m), 492 (m) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε, $M^{-1}cm^{-1}$) = 375 (19180), 655 (236) nm. MS (ESI+): m/z = 1127 $[Cu_4(\mu_4\text{-}O)(\mathbf{L^1})Cl_3]^+$. $C_{38}H_{62}Cl_4Cu_4N_4O_5Si_4$ (1163.3): calcd. C 39.23, H 5.37, N 4.81; found C 39.02, H 5.19, N 4.70.

HL^2: A mixture of trimethylsilyl *p*-aminobenzoate (0.90 g, 4.00 mmol) and 2,6-diformyl-4-methylphenol (0.33 g, 2.00 mmol) in methanol/chloroform (2:1 v/v, 20 mL) was heated to reflux for 4 h and then cooled to room temperature. The solvent was removed under reduced pressure to produce an orange solid, which was washed with methanol (10 mL) and diethyl ether (10 mL) and dried in air, yield 1.05 g (90.0%). FTIR (KBr): $\tilde{\nu}$ = 3470 (w), 3373 (w), 2955 (m), 2907 (m), 1713 (vs), 1626 (s), 1582 (vs), 1460 (m), 1414 (m), 1358 (m), 1312 (vs), 1248 (vs), 1207 (s), 1169 (s), 1111 (s), 1101 (s), 1040 (w), 984 (m), 853 (vs), 772 (s), 758 (s), 700 (m), 669 (m), 608 (w), 573 (w), 567 (w), 523 (w), 511 (w), 463 (vw), 401 (vw) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 13.56 (s, 1 H, O*H*), 8.83 (s, 2 H, -C*H*=N), 8.08 (d, J = 8.86 Hz, 4 H, Ar-*H*), 7.77 (s, 2 H, Ar-*H*), 7.29 (d, J = 8.17 Hz, 4 H, Ar-*H*), 4.07 (s, 4 H, CH_2), 2.40 (s, 3 H, CH_3), 0.17 (s, 18 H, CH_3) ppm.

$[Cu_4(\mu_4\text{-}O)(\mathbf{L^2})_2Cl_4]$ (2): A solution of $CuCl_2{\cdot}2H_2O$ (0.34 g, 2.00 mmol) in methanol (5 mL) was added dropwise to a solution of $\mathbf{HL^2}$ (0.58 g, 1.00 mmol) in methanol/chloroform (1:1, 5 mL), then triethylamine (three drops) was added and the mixture was stirred at 50 °C for 2 h. The solution became dark-green. After slow evaporation of the solvent at room temperature, a dark-green crystalline precipitate was filtered off, washed with methanol/chloroform (1:1, 5 mL) and dried in air. The crude product was purified by column chromatography (CH_2Cl_2/MeOH, 99:1), yield 0.34 g (23.0%). Crystals suitable for X-ray diffraction were obtained directly from the reaction mixture after 5 days by slow evaporation of the solvent at room temperature. $C_{62}H_{74}Cl_4Cu_4N_4O_{11}Si_4$ (1559.6): calcd. C 47.75, H 4.78, N 3.59; found C 47.67, H 4.64, N 3.62. FTIR (KBr): $\tilde{\nu}$3416 (m), 3061 (vw), 2955 (m), 2922 (w), 2903 (w), 1711 (vs), 1624 (vs), 1587 (s), 1543 (vs), 1502 (m), 1420 (m), 1398 (m), 1346 (m), 1315 (vs), 1306 (vs), 1250 (vs), 1196 (m), 1175 (s), 1109 (s), 1082 (s), 1018 (m), 1001 (w), 980 (w), 955 (w), 856 (vs), 766 (s), 702 (m), 663 (vw), 623 (w), 557 (w), 496 (m), 417 (w) cm^{-1}.

UV/Vis ($CHCl_3$): λ_{max} (ε, $M^{-1}\,cm^{-1}$) = 384 (38300), 415 (38060), 745 (550) nm. MS (ESI+): m/z = 1561 $[M + H]^+$, 637 $[Cu(\mathbf{HL^2})]^{2+}$.

Physical Measurements: FTIR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer, in transmission mode at room temperature with a resolution of 2 cm^{-1} and 32 scans. The samples were measured in dry KBr as pellets. UV/Vis spectra were recorded with Analytik Jena SPECORD 200 spectrophotometer using a quartz cuvette of 1 cm path length. Elemental CHN analyses were performed with a Perkin–Elmer CHNS 2400 II elemental analyser. Electrospray ionisation mass spectrometry (ESI-MS) was carried out with a Bruker Esquire 3000 instrument, and the samples were dissolved in methanol.

Magnetic measurements were carried out on microcrystalline samples with a Quantum Design SQUID magnetometer (MPMS-XL). Variable-temperature (2–300 K) direct current (dc) magnetic susceptibility was measured under an applied magnetic field of 0.1 T. All data were corrected for the contribution of the sample holder and diamagnetism of the samples estimated from Pascal's constants.[58,31]

Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation. The single crystals were positioned at 40 mm from the detector and 398 and 149 frames were measured each for 60 and 250 s over 1° scan width for **1** and **2**, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.[59] The structures were solved by direct methods using Olex2 software[60] with the SHELXS structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-97.[61] Atomic displacements for non-hydrogen atoms were refined by using an anisotropic model. Hydrogen atoms were placed in calculated positions, riding on their carrier atoms. Some atoms of silane and siloxane fragments were found to be severely disordered and their positional parameters were refined in combination with PART and SADI restraints by using anisotropic/isotropic model for non-H atoms. To improve the result, the X-ray data collection for compound **2** was repeated for a series of single-crystals, but all of them were weakly diffracting and the resolution of the collected X-ray data was estimated to be 1.2 Å. Nevertheless, the structure could be solved and electron density of the molecule was well defined, allowing for the determination of the atomic connectivity. The model of the structure was refined with anisotropic temperature factors for Cu, Si and Cl atoms and isotropic for the remaining atoms. The molecular plots were obtained by using the Olex2 program. The main crystallographic data together with refinement details are summarised in Table 4.

Table 4. Crystallographic data and details of data collection and structure refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_{38}H_{62}Cl_4Cu_4N_4O_5Si_4$	$C_{62}H_{74}Cl_4Cu_4N_4O_{11}Si_4$
Formula weight	1163.24	1559.57
Temperature [K]	200	200
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pbca*
a [Å]	10.6197(4)	18.4724(19)
b [Å]	15.8891(6)	21.1291(14)
c [Å]	17.5376(7)	37.551(4)
α [°]	108.993(4)	
β [°]	106.006(3)	
γ [°]	93.562(3)	
V [Å^3]	2651.84(18)	14656(2)
Z	2	8
$D_{calcd.}$ [mg/mm^3]	1.457	1.414
μ [mm^{-1}]	1.915	1.412
Crystal size [mm^3]	0.02 × 0.02 × 0.20	0.02 × 0.10 × 0.15
$\theta_{min.}$, $\theta_{max.}$ [°]	6.06 to 52	4.82 to 37.68
Reflections collected	22810	19335
Independent reflections	10818 [R_{int} = 0.0443]	5746 [R_{int} = 0.1726]
Data/restraints/parameters	10818/42/533	5746/25/447
R_1[a] [$I > 2\sigma(I)$]	0.0696	0.0778
wR_2[b] (all data)	0.01715	0.1630
GOF[c]	1.028	0.989
Largest diff. peak/hole [e Å^{-3}]	0.92/–0.92	0.63/–0.58

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2$ = $\{\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[w(F_o^2)2]\}^{1/2}$. [c] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

CCDC-1005531 (for **1**) and -1005532 (for **2**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic Studies, Typical Procedures and Product Analysis

Hydrocarboxylation; Typical Procedure: Experiments were performed by following a previously developed protocol.[36] To **1** or **2** (4.0 μmol) in a 13.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar, were added $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL), MeCN (4.0 mL) (total solvent volume was 6.0 mL), and alkane (1.00 mmol). The autoclave was closed and flushed with CO three times to remove the air, and finally pressurised with 20 atm of CO. ***CAUTION:*** *Due to the toxicity of CO, all operations should be carried out in a well-ventilated hood!* The reaction mixture was typically stirred at 60 °C for 4 h by using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask. Diethyl ether (9.0 mL) and cycloheptanone (90 μL; typical GC internal standard) were added. In the case of cycloheptane hydrocarboxylation, cyclohexanone (90 μL) was used as internal standard instead of cycloheptanone. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analysed by GC, revealing the formation of the corresponding monocarboxylic acids as the dominant products. Control experiments indicated that the hydrocarboxylations also proceed in the metal-free systems, although typically leading to 2 to 5 times inferior yields of carboxylic acids in comparison with the Cu-catalysed transformations.[36] The formation of dicarboxylic acids was not observed by GC–MS analysis.

Peroxidative Oxidations: The oxidation of cyclohexane with aqueous H_2O_2 was carried out in air in round-bottomed flasks with vigorous stirring, using MeCN as solvent (up to 5.0 mL total volume). ***CAUTION:*** *A mixture of H_2O_2 with organic compounds is potentially explosive!* Catalyst precursors **1** or **2** and trifluoroacetic acid (TFA, optional), in the form of a stock solution in acetonitrile, were introduced into the reaction mixture. Cyclohexane (0.25 mL, 2.3 mmol) was then introduced, and the reaction was started when hydrogen peroxide (50% in H_2O, 0.68 mL, 11 mmol) was added in one portion. The concentrations of the reactants in the reaction mixture were as follows: catalyst precursor (5×10^{-4} mol L^{-1}), TFA (0.005 mol L^{-1}), substrate (0.46 mol L^{-1}), and H_2O_2 (2.2 mol L^{-1}). The reaction mixture was stirred at 50 °C for 2 h and an aliquot was taken at 5, 15, 30, 45, 60 and 120 min, and analysed by GC using nitromethane (50 μL) as an internal standard. Before the GC analysis an excess of triphenylphosphine was added to reduce the formed cyclohexyl hydroperoxide to the corresponding alcohol, and hydrogen peroxide to water, following a method developed by Shul'pin.[38] Attribution of peaks was made by comparison with

chromatograms of authentic samples. Control experiments were performed with different amounts of H_2O_2 and other reagents, and confirmed that no product of cyclohexane oxidation was obtained unless the metal catalyst was used.

Microwave-Assisted Solvent-Free Peroxidative Oxidations: Catalytic tests with 1-phenylethanol were performed with a focused Anton Paar Monowave 300 reactor using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector. The alcohol (2.5 mmol), catalyst precursor **1** or **2** (5 μmol, 0.2 mol-% vs. substrate) and a 70% aqueous solution of *t*BuOOH (5 mmol) were introduced in a cylindric Pyrex tube that was sealed. This tube was then placed in the microwave reactor and the system was stirred under irradiation (5 or 20 W) at 80 or 120 °C for 0.5–3 h. After cooling to room temperature, benzaldehyde (150 μL, internal standard) and MeCN (2.5 mL; to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC using the internal standard method.

Gas chromatographic analyses were carried out with a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) (He as the carrier gas), using the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature of the column was maintained at 100 °C (oxidation of cyclohexane) or 120 °C (hydrocarboxylations of alkanes and oxidation of alcohol) for 1 min, then raised 10 °C/min to 180 °C (oxidation of cyclohexane) or 200 °C (hydrocarboxylations of alkanes and oxidation of alcohol), and held at this temperature for 1 min. Attribution of peaks was made by comparison with chromatograms of genuine samples and, in some cases, by GC–MS analyses with a Perkin–Elmer Clarus 600 C instrument (He as the carrier gas), equipped with a 30 m × 0.22 mm × 25 μm BPX5 (SGE) capillary column.

The catalytic tests under MW irradiation were performed with a focused Anton Paar Monowave 300 reactor using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector.

Supporting Information (see footnote on the first page of this article): View of the complex along the normal to Cu3–O1–O3–Cu4 plane (Figure S1), eigenvalues of the isotropic spin-Hamiltonian (1) relative to $E_{S=0}$[6], with the parameters defined in the text for **1**, as a function of the total spin quantum number S (Figure S2).

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