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Electronic Supplementary Information (ESI)

New Diamandoid-like $[Cu_3B(\mu\text{-}O)_6]$ Core Self-assembled from Bis-Tris Biobuffer for Mild Hydrocarboxylation of Alkanes to Carboxylic Acids

Alexander M. Kirillov,*[a] Yauhen Y. Karabach,[a] Marina V. Kirillova,[a] Matti Haukka[b] and Armando J. L. Pombeiro*[a]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Avenida Rovisco Pais, 1049-001 Lisbon, Portugal. E-mail: kirillov@ist.utl.pt, pombeiro@ist.utl.pt; Fax: 351 218464455*
[b] *Department of Chemistry, University of Eastern Finland, P.O. Box 111, FIN-80101 Joensuu, Finland.*

ESI contains full experimental details including general methods, alkane hydrocarboxylations and X-ray crystal structure determination procedures, supplementary references, supplementary figures with structural representations of **1** (Figs. S1−S3) and the proposed reaction mechanism for alkane hydrocarbohylations (Fig. S4), as well as supporting Table S1 with selected bonding parameters in **1** and an extended version of Table 1 (Table S2) with the structural formulae of isomeric carboxylic acid products and further details on alkane hydrocarboxylations.

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1. Full Experimental Details

General Methods. All synthetic work was performed in air and at room temperature. All chemicals were obtained from commercial sources and used as received. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ESI-MS(±) spectra were run on a 500-MS LC Ion Trap instrument (Varian Inc, Alto Palo, CA, USA) equipped with an electrospray (ESI) ion source, using ca. 10^{-3} M solutions of **1** in methanol. Gas chromatography (GC) analyses were performed on a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX (J&W) capillary column (30 m × 0.25 mm × 0.25 μm; helium carrier gas) and by using Jasco-Borwin v.1.50 software. In some cases, carboxylation products were also identified by (i) ESI-MS spectrometry (500-MS LC Ion Trap instrument, Varian Inc, Alto Palo, CA, USA) using further diluted MeCN/Et_2O solutions of the reaction mixtures with ca. 10^{-3} M of carboxylic acids and (ii) ^{1}H and ^{13}C-{^{1}H} NMR techniques (Bruker Avance II 300, UltraShield™ Magnet spectrometer) using further diluted with MeCN-d_3 solutions of the reaction mixtures.

Alkane Hydrocarboxylations. In a typical experiment the reaction mixtures were prepared as follows: to 4.0 μmol of the copper promoter **1** contained in a 13.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar, were added 1.00–1.50 mmol of $K_2S_2O_8$, 2.0 mL of H_2O, 4.0 mL of MeCN (typical total solvent volume was 6.0 mL) and 1.00 mmol of alkane (if liquid). Then the autoclave was closed and flushed with CO three times to remove the air, and finally pressurized with 0.75−1.0 atm of alkane (if gaseous) and 10–20 atm of CO. The reaction mixture was stirred for 6 h at 60 °C 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 (9.0–11.0 mL) and 90 μL of cycloheptanone (GC internal standard) were added. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by gas chromatography (internal standard method), revealing the formation of the corresponding monocarboxylic acids as the dominant products. In the reactions with cycloalkane substrates, cyclic ketones and alcohols were also formed as by-products of partial alkane oxidation, whereas in the transformations of linear alkanes the generation of the corresponding oxygenates was negligible (their overall yields were not exceeding 1.0%).

Blank tests indicated that the hydrocarboxylations also proceed in the metal-free systems,[11] although typically leading to 2-4 times inferior yields of carboxylic acids in comparison with the Cu-promoted transformations. Additional experiments were performed under the typical reaction conditions in the presence of the carbon-centred radical trap $CBrCl_3$, revealing the suppression of

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the formation of carboxylic acids. The acetonitrile solvent is nonreactive in the present systems, since no generation of acetic or propionic acids from MeCN was detected when the reactions were repeated in the absence of alkane. Furthermore, the alkane hydrocarboxylations do not proceed either in sole H_2O or MeCN solvent.

X-ray Crystallography. The X-ray quality single crystals of **1** were mounted in inert oil within the cold gas stream of the diffractometer. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer at 120 K. The Denzo–Scalepack[S1] program package was used for cell refinements and data reduction. The structure was solved by direct methods by using the SHELXS-97 program.[S2] A multiscan absorption correction based on equivalent reflections (SADABS v.2.10)[S3] was applied to all data. The structure was refined with SHELXL-97[S2] and the WinGX graphical user interface.[S4] The O5 and B2 atoms were restrained so that their U^{ij} components approximate to isotropic behavior. The OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq}(parent atom). The hydrogen atoms of the O7 and O8 were disordered over several positions. Due to the disorder these hydrogen atoms were omitted. However, they were taken into account in the unit-cell content. Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C−H = 0.99 Å, and U_{iso} = 1.2 U_{eq}(parent atom).

2. Supplementary References

S1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology, Macromolecular Crystallography, Part A* (Eds.: C. W. Carter Jr. and R. M. Sweet), Academic Press, New York, **1997**; vol. 276, pp. 307– 326.

S2 G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112;

S3 G. M. Sheldrick, *SADABS, Version 2.10*, Bruker Axs, Madison, WI, **2003**.

S4 L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

3. Supplementary Figures and Tables

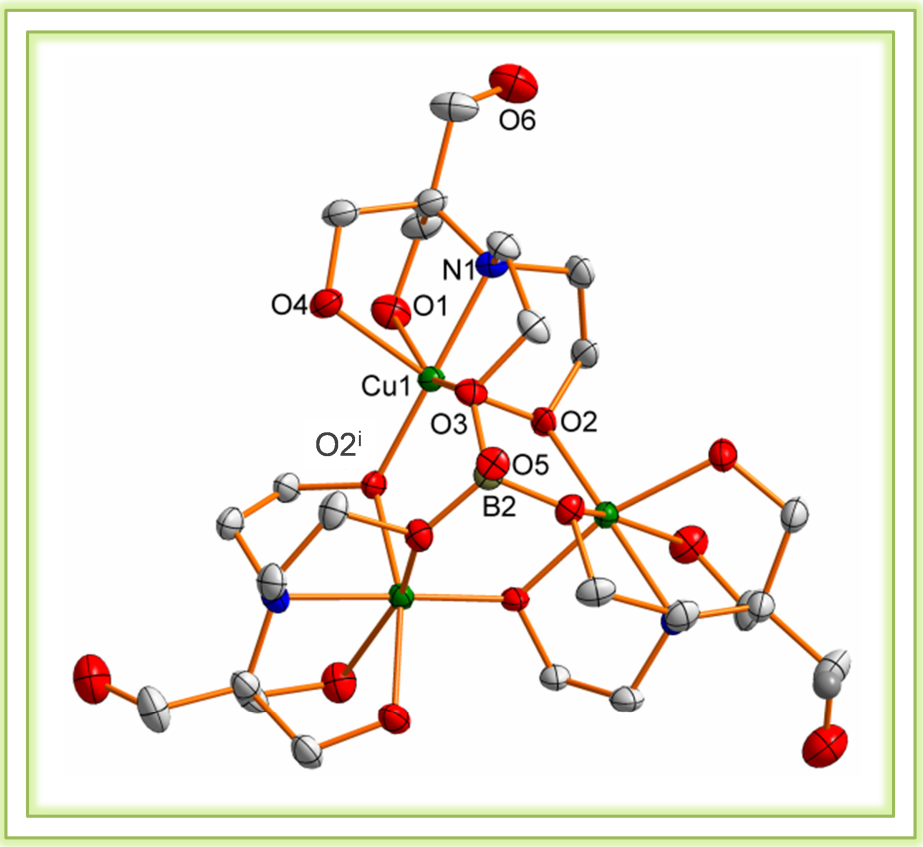

Fig. S1 Ellipsoid plot of $[Cu_3(\mu_3\text{-}BO)(H_3L)_3][BF_4]\cdot 2H_2O$ (**1**) with the partial atom labeling scheme (displacement ellipsoids are drawn at the 50% probability level). H atoms, BF_4^- anions and crystallization water molecules are omitted for clarity. Colour codes: Cu green, B dark green, O red, N blue, C gray. Symmetry code (i): −x+3/2, −y+1, z+1/2.

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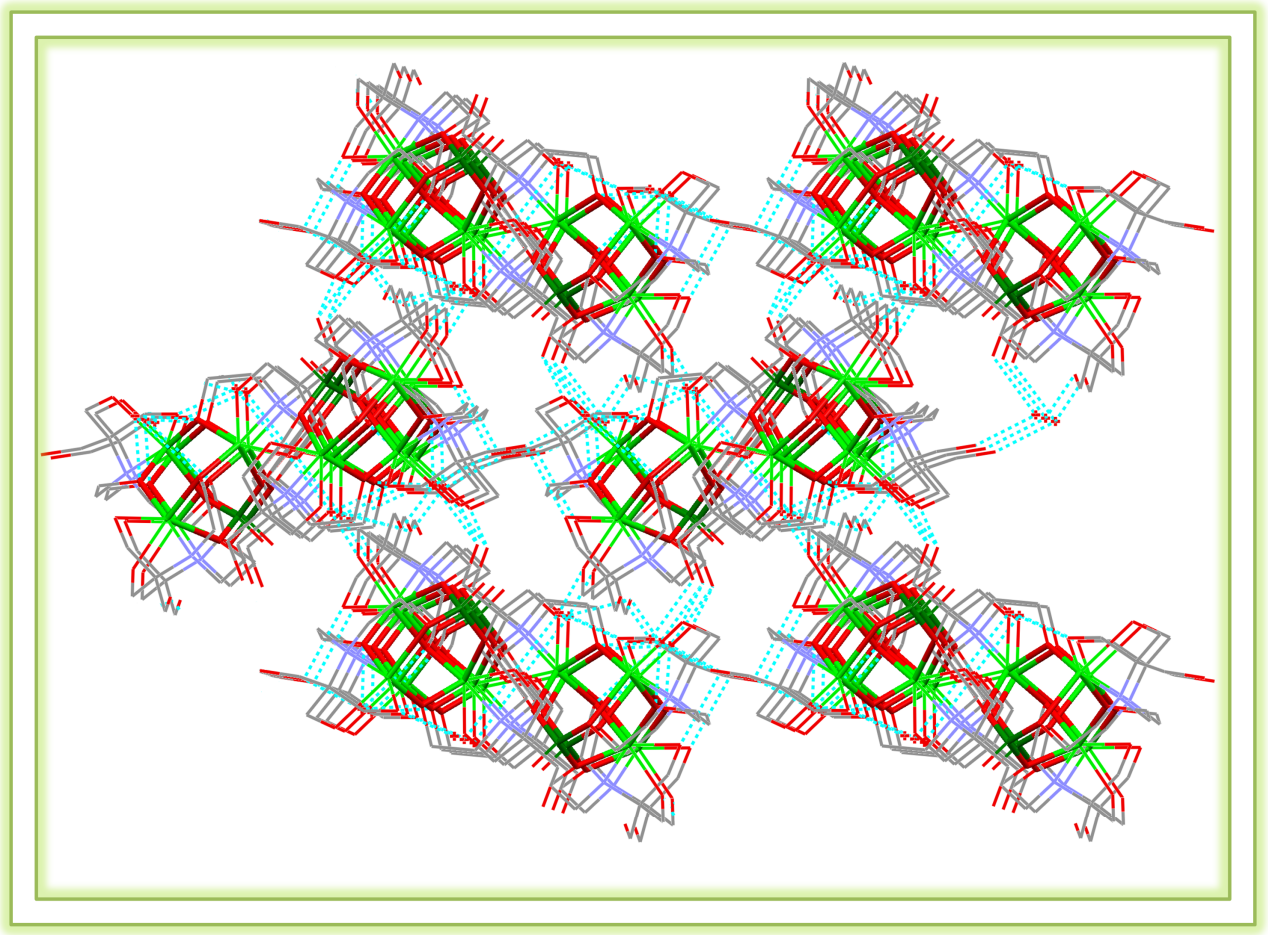


Fig. S2 Fragment of the crystal packing diagram (rotated view along the *a* axis) of **1** showing the linkage of the adjacent $[Cu_3(\mu_3\text{-}BO)(H_3L)_3]^+$ cluster units by multiple hydrogen bonds (blue dotted lines) generating a 3D supramolecular network. The $[Cu_3B(\mu\text{-}O)_6]$ cores are shown as capped sticks. H atoms and BF_4^- anions are omitted for clarity. Colour codes: Cu green, B dark green, O red, N blue, C gray.

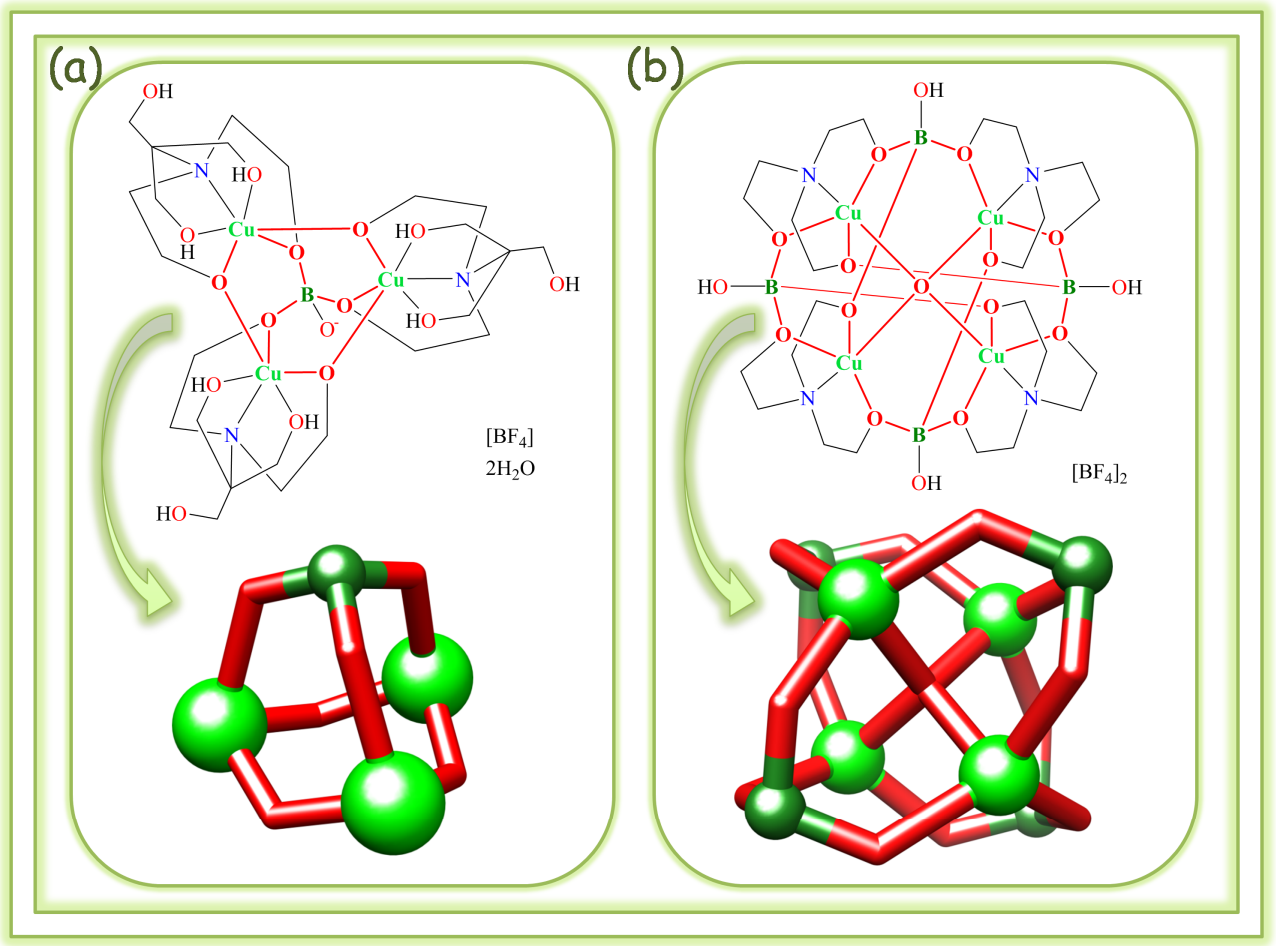


Fig. S3 Comparative representation of multicopper(II) complexes: (a) $[Cu_3(\mu_3\text{-}BO)(H_3L)_3][BF_4]\cdot 2H_2O$ (**1**) and (b) $[O\subset Cu_4(\mu_3\text{-}BOH)_4\{N(CH_2CH_2O)_3\}_4][BF_4]_2$,[6a] and their unprecedented boron-driven $[Cu_3B(\mu\text{-}O)_6]$ (a) and $[Cu_4B_4(\mu_4\text{-}O)(\mu\text{-}O)_{12}]$ (b) cores derived via aqueous medium self-assembly from copper(II) nitrate, $NaBF_4$, NaOH and either Bis-Tris (a) or triethanolamine (b). This figure also shows how a slight modification of an aminopolyalcohol ligand leads to structurally distinct products, which represent the unique derivatives wherein B and Cu centres are multiply ligated though bridging oxygen atoms.

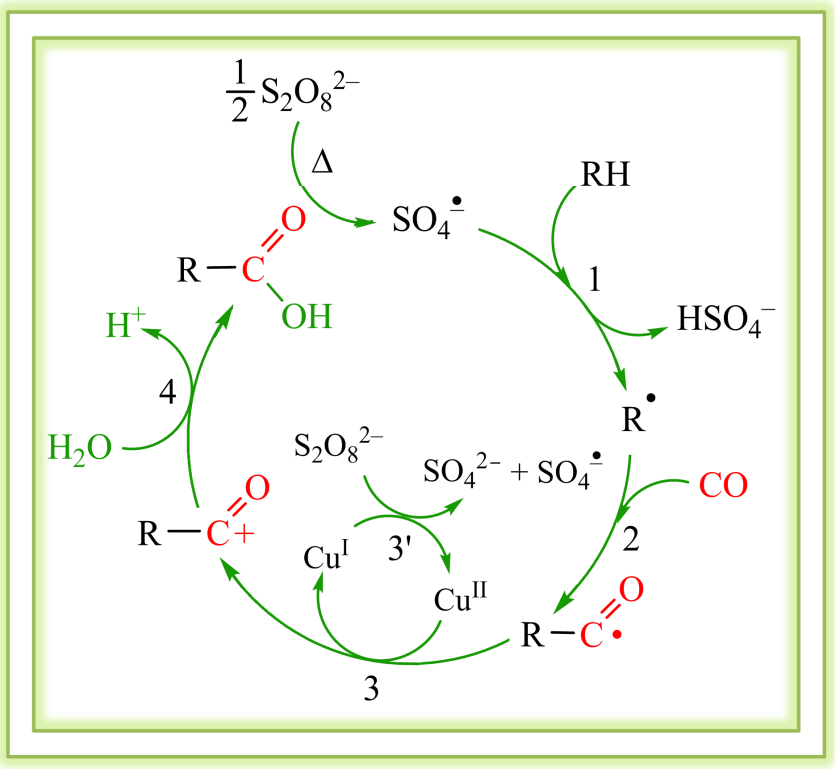


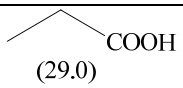
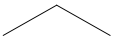
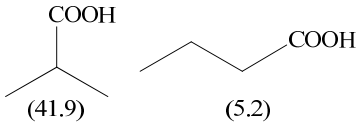
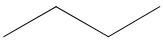
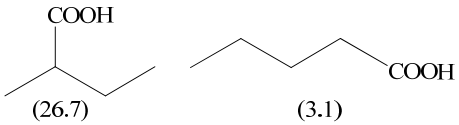
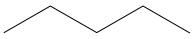
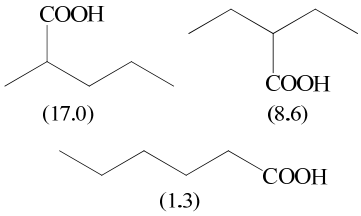
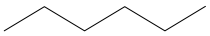
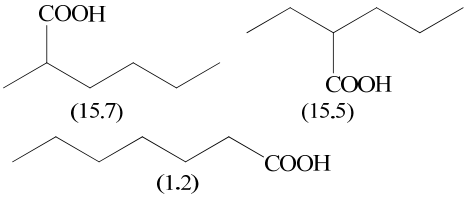
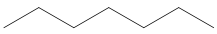
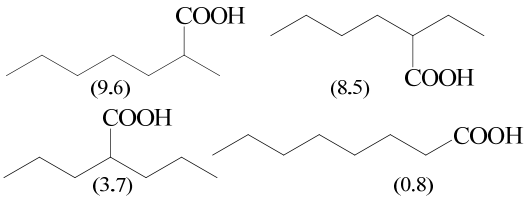
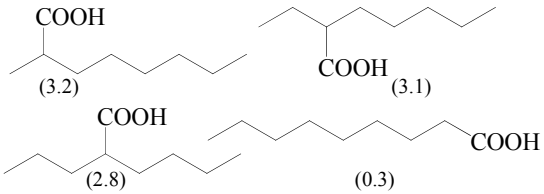
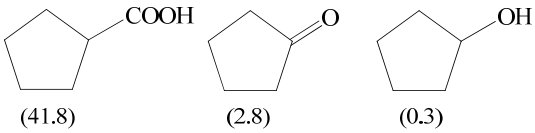
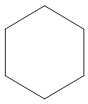
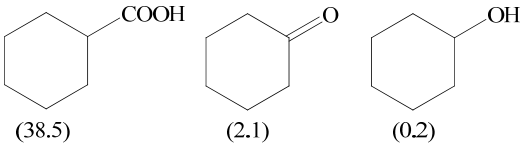
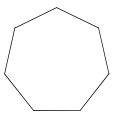
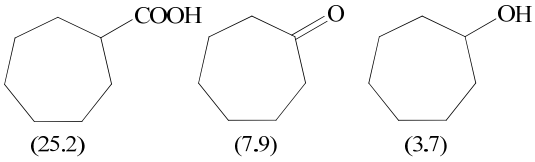
Fig. S4 Proposed mechanism for the copper-promoted hydrocarboxylation of alkanes (RH) to carboxylic acids (RCOOH).

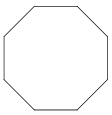
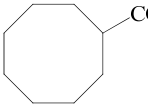
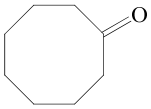
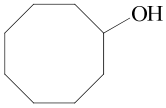
Table S1. Selected bond lengths (Å) and angles (deg) for **1**[a]

Cu(1)−O(1)	2.435(3)	Cu(1)−O(4)	2.047(3)
Cu(1)−O(2)	1.959(3)	Cu(1)−N(1)	2.013(3)
Cu(1)−O(2)^{i}	1.896(3)	B(2)−O(3)	1.454(4)
Cu(1)−O(3)	2.276(3)	B(2)−O(5)	1.417(8)
O(2)−Cu(1)−N(1)	84.78(13)	N(1)−Cu(1)−O(1)	79.16(12)
O(2)−Cu(1)−O(4)	164.45(12)	O(4)−Cu(1)−O(1)	75.71(12)
N(1)−Cu(1)−O(4)	81.38(13)	O(2)^{i}−Cu(1)−O(2)	93.07(17)
O(2)−Cu(1)−O(3)	92.39(11)	O(2)^{i}−Cu(1)−O(4)	99.80(12)
O(3)−Cu(1)−O(1)	160.25(10)	O(2)^{i}−Cu(1)−O(3)	103.80(11)
N(1)−Cu(1)−O(3)	83.20(13)	O(2)^{i}−Cu(1)−O(1)	94.17(11)
O(4)−Cu(1)−O(3)	92.98(11)	O(2)^{i}−Cu(1)−N(1)	172.77(14)
O(2)−Cu(1)−O(1)	94.78(11)	Cu(1)^{ii}−O(2)−Cu(1)	125.15(14)

[a]Symmetry codes: (i): −x+3/2, −y+1, z+1/2; (ii) x−1/2, −y+3/2, −z+1.

Table S2. Extended version of Table 1. Cu-promoted (by **1**) single-pot hydrocarboxylation of C_n alkanes into C_{n+1} carboxylic acids.[a]

Entry	Alkane	Carboxylic acid product (yield, %)[b]	Total yield (%)[c] [Selectivity][d]
1		 (29.0)	29.0
2		 (41.9) (5.2)	47.1 [1°:2° = 1:24]
3		 (26.7) (3.1)	30.0 [1°:2° = 1:13]
4		 (17.0) (8.6) (1.3)	26.9 [C(1):C(2):C(3) = 1:20:20]
5		 (15.7) (15.5) (1.2)	32.4 [C(1):C(2):C(3) = 1:20:19]
6		 (9.6) (8.5) (3.7) (0.8)	22.6 [*C*(1):*C*(2):*C*(3): :*C*(4)] = 1:18:16:14
7		 (3.2) (3.1) (2.8) (0.3)	9.4 *C*(1):*C*(2):*C*(3): :*C*(4) = 1:16:15:14
8[e]		 (41.8) (2.8) (0.3)	44.9
9[e]		 (38.5) (2.1) (0.2)	40.8
10[e]		 (25.2) (7.9) (3.7)	36.8

11[e]		 (9.0)	 (9.3)	 (4.4)	22.7

[a]Reaction conditions: *p*(gaseous alkane) = 1.0 (C_2H_6, C_3H_8) or 0.75 (*n*-C_4H_{10}) atm + *p*(CO) = 10 atm (1 atm = 0.266 mol); liquid alkane (1.0 mmol) + *p*(CO) = 20 atm; compound **1** (4.0 μmol); $K_2S_2O_8$ = 1.0 (entries 1−3) or 1.5 (entries 4−11) mmol; H_2O (2.0 mL)/MeCN (4.0 mL); 60 ºC, 6 h, 13.0 mL autoclave. [b]Moles of product/100 moles of alkane. [c]Yield of all products; in transformations of linear C_2−C_8 alkanes, the yields of ketones and alcohols are negligible (<1%) and thus are not indicated herein. [d]Whenever applicable, selectivity parameters are indicated: 1º:2º and *C*(1):*C*(2):*C*(3):*C*(4) stand for bond selectivity and regioselectivity, meaning the normalized (for the relative number of H atoms) reactivities of hydrogen atoms at primary and secondary carbon atoms of alkanes, or at different positions of linear alkane chains, respectively. [e]Cyclic ketones and alcohols are also formed as products of oxidation.