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Solvent-free microwave-assisted peroxidative oxidation of secondary alcohols to the corresponding ketones catalyzed by copper(II) 2,4-alkoxy-1,3,5-triazapentadienato complexes

Paweł J. Figiel,[a] Maximilian N. Kopylovich,[a] Jamal Lasri,[a] M. Fátima C. Guedes da Silva,[a,b]
João J. R. Fraústo da Silva,[a] and Armando J. L. Pombeiro*[a]

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[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049-001, Lisbon, Portugal. Fax: +351 218464455; E-mail: pombeiro@ist.utl.pt*
homepage: http://cqe.ist.utl.pt/research/group5.php
[b] *Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon, Campo Grande 376, 1749-024 Lisbon, Portugal*

1. General Materials and Instrumentation

All the chemicals were obtained from commercial sources and used as received. Infrared spectra (4000-400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software. Electrospray mass spectra were carried out with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. The solutions in acetone were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 μL/min. The drying gas temperature was maintained at 350 ºC and dinitrogen was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from *m/z* = 50 to 1500. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, operating at 10 W) which is fitted with a rotational system and an IR detector of temperature.

2. Synthesis of catalysts (copper(II) 2,4-alkoxy-1,3,5-triazapentadienates)

The complexes were prepared as shown below by using a more general and modified procedure based on that reported[13] for **1**. Thus, refluxing with stirring a mixture of copper(II) nitrate $Cu(NO_3)_2•2.5H_2O$ (231.9 mg, 1 mmol) and sodium dicyanamidate (89.0 mg, 2 mmol) in the corresponding alcohol (MeOH for **1** or EtOH for **2**, 5 mL) gives a green precipitate in *ca*. 10 min. After 1 h of refluxing, *n*-prolyamine (4 equiv to copper(II) nitrate) is added, and after *ca*. 1 h the reaction solution is red and a colourless precipitate released (analysis of this precipitate indicates that it is $NaNO_3$). This solid is filtered off after 12 h of refluxing, and the filtrate, containing **1** or **2**, is taken to dryness *in vacuo* at 20–25 °C. Recrystallization from a water/acetone (1:10) mixture allows to obtain the pure complex **1** or **2.** Recrystallization of **1** or **2** from methanol or ethanol, correspondingly, gives dark red crystals suitable for X-ray structural analyses.

[Cu{HN=C(OMe)NC(OMe)=NH}$_2$] (1). Yield 91 %. Anal. Calcd for $C_8H_{16}CuN_6O_4$: C, 29.67; H, 4.98; N, 25.95. Found C, 30.06; H, 4.92; N, 26.11. ESI$^+$-MS (in acetone), *m/z*; 324 $[M + H]^+$. IR (KBr, selected bands, cm^{-1}): 3359 (s), 3342 (s) ν(NH); 2992(m-w), 2954 (m-w) ν(CH); 1609 (s) ν(C=N); 1563 (s) δ(NH). The identity of **1** was also confirmed by X-ray after its recrystallization from MeOH [*P*21/*n* (no. 14), a = 10.018(3), b = 5.6635(14), c = 11.632(3) Å, β = 99.703(6)°, V = 650.6(3) Å^3]^{13b}.

[Cu{HN=C(OEt)NC(OEt)=NH}$_2$] (2). Yield 85 %. Anal. Calcd for $C_{12}H_{24}CuN_6O_4$: C, 37.94; H, 6.37; N, 22.12. Found C, 38.12; H, 6.31; N, 22.00. ESI$^+$-MS (in acetone), *m/z*; 380 [M + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3336 (s), 3306 (s) ν(NH); 2981 (s), 2928 (m-w) ν(CH); 1608 (s) ν(C=N); 1536 (s) δ(NH).

3. Details of the X-ray crystal structure analysis and refinement

Single crystals of **1** and **2** were obtained as indicated above. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data were collected at 296 K (**2**) using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [1S] on all the observed reflections. Absorption corrections were applied using SADABS.[1S] Structures were solved by direct methods by using the SHELXS–97 package[2S] and refined with SHELXL–97.[3S] Calculations were performed using the WinGX System–Version 1.80.03.[4S] All hydrogens were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non–hydrogen atoms and isotropic for the remaining atoms were employed. Table 1 contains the crystallographic parameters for the described crystals. CCDC 752593 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1S] Bruker, *APEX2 & SAINT. Bruker*, AXS Inc., Madison, Wisconsin, USA, 2004.
[2S] G. M. Sheldrick, *Acta Crystallogr*. *Sect. A*, **1990**, *46*, 467.
[3S] G. M. Sheldrick, *Acta Crystallogr*. *Sect. A*, **2008**, *A64*,112.
[4S] L. J. Farrugia, *J. Appl. Crystallog.* **1999**, *32*, 837.

4. Experimental details of catalytic activity studies

Microwave-assisted reactions: The alcohol substrate (5 mmol), TBHP (10 mmol) and the copper(II) triazapentadienato complex **1** or **2** (0.01 mmol) were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under stirring and irradiation for 5, 15, 30, 60 or 240 min at 50 or 80 ºC, depending on the alcohol used. After the reaction, the mixture was allowed to cool down. The power of 10 W was selected for all experiments, since we have found that 5 W is not sufficient to maintain the desired reaction temperature, and a higher power (*e.g.* 20 W) does not significantly affect the product yield.

Conventional method: Oxidation reactions were carried out in 50 mL round-bottom flasks equipped with a condenser. Under typical conditions, the copper(II) triazapentadienato complex **1** or **2** (0.01 mmol) was added to the flask, followed by the alcohol (5 mmol) and TBHP (10 mmol). The reaction solutions in all cases were vigorously stirred using magnetic stirrers. The desired reaction temperature (in the 40–80 ºC range) was achieved using an oil bath.

GC analysis: Samples after reactions were treated with 5 mL of MeCN and 300 μL of benzaldehyde (internal standard). After mixing, aliquots were placed into *Eppendorf* vials, diluted with Et_2O (*ca.* 10 times) and centrifuged. For GC analysis, 0.4 μl of sample was injected into the column.

5. Supporting catalytic (for complex 1) and structural figures, and selected bonding parameters (for complex 2)

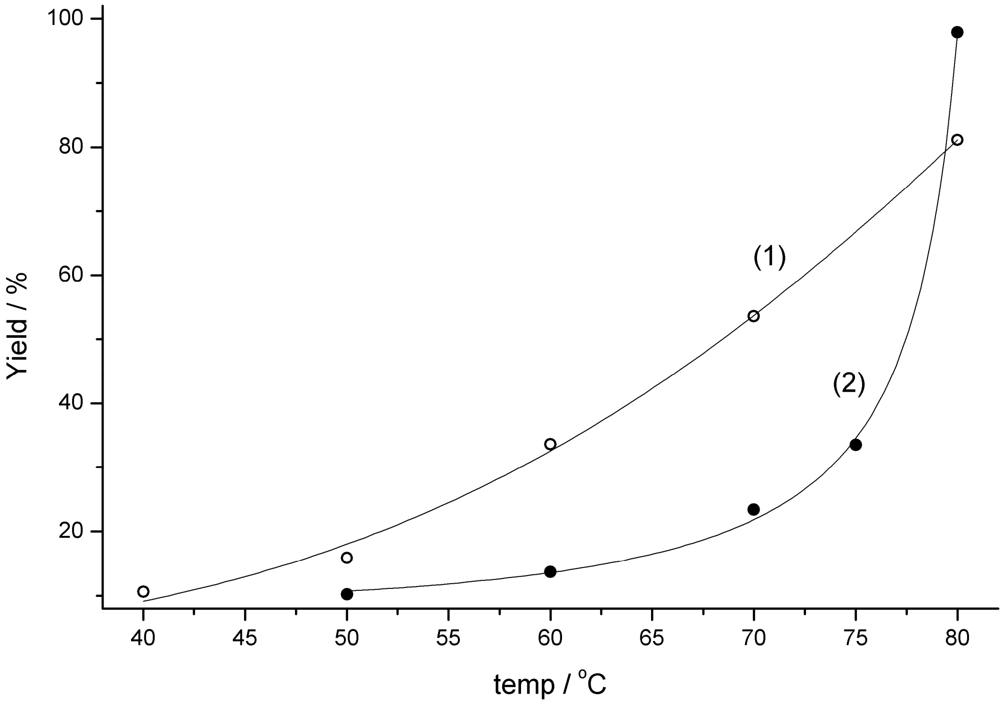

Figure S1. Effect of temperature on the acetophenone yield, using compound **1** as catalyst: (1) conventional, 300 min; (2) MW assisted, 30 min. For other conditions see Table 1.

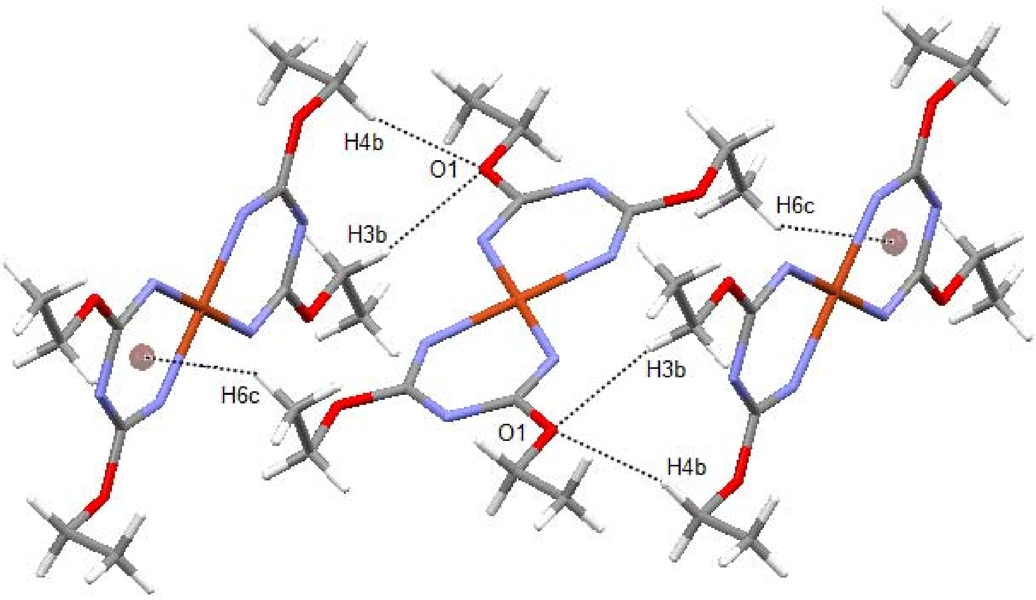

Figure S2. Representation of the intermolecular C6–H6c–π interactions in compound **2**, involving the C6 methyl group and an adjacent metallacycle ring (the centroid of the metallacycle ring is represented as a dot), and the inter-molecular hydrogen bond: D–H···A [d(D···A) Å; ∠(DHA) °]:

C3–H3b···O1^{i} [3.486(4) Å, 165.00 º], C4–H4b···O1^{i} [3.507(4) Å, 163.00 º]. Symmetry operation to generate equivalent atoms (*i*) x,-1/2-y,1/2+z

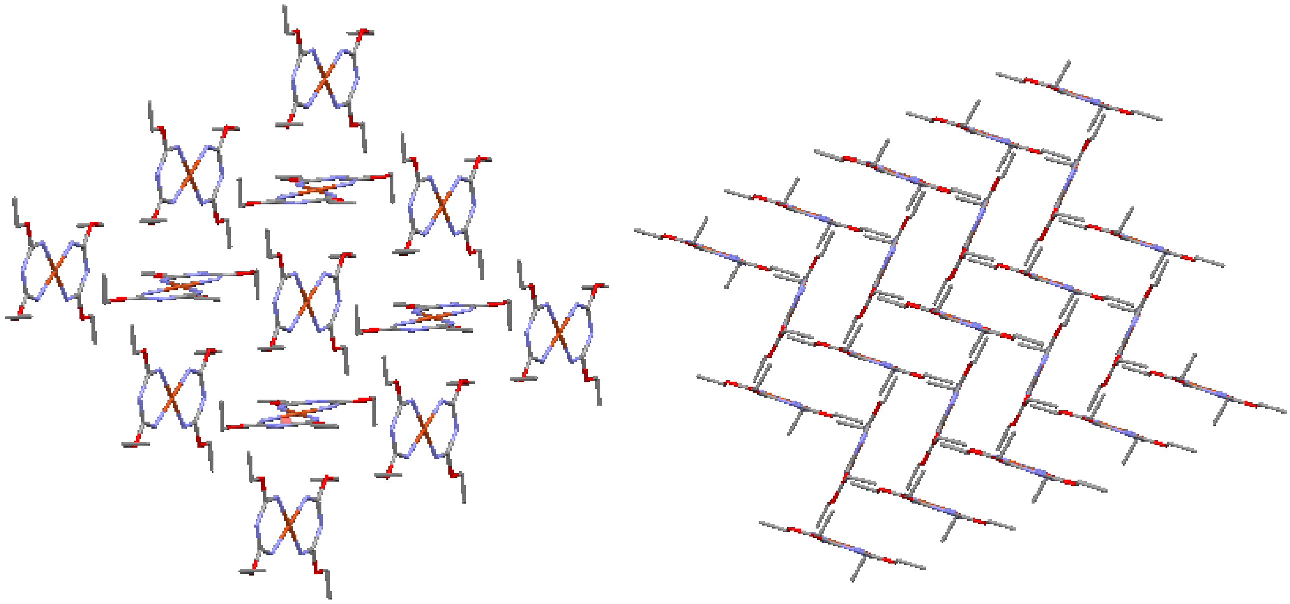

Figure S3. Fragment of the crystal packing diagram of **2** (arbitrary views) showing the relative arrangement of the molecules in two layers relatively displaced by an angle of ca. 83.35 º.

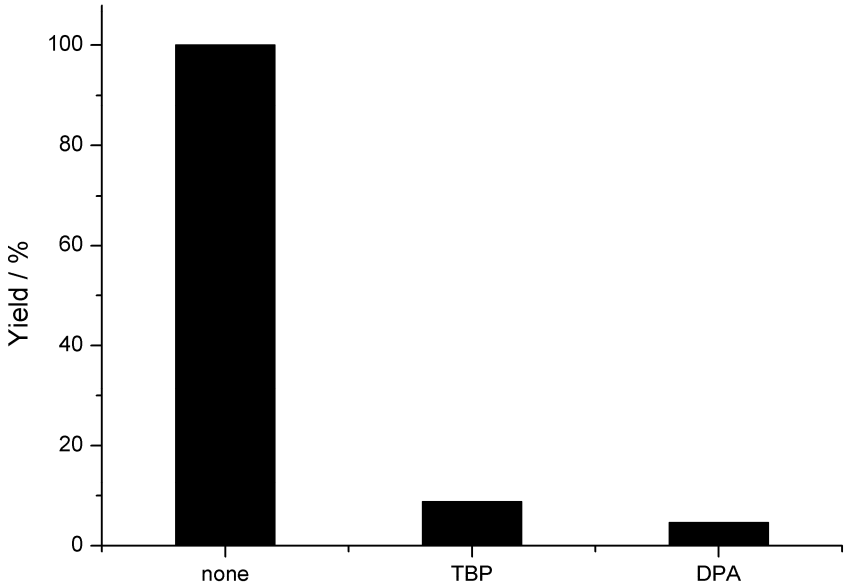

Figure S4. Effect of radical traps (1:1 mol ratio *vs.* substrate) on the acetophenone yield, using compound **1** as catalyst (TBP = *2,4,6*-tri-*tert*-butylphenol, DPA = diphenylamine). Conditions: MW irradiation, 30 min., 80^{o}C; for other conditions see Table 1.

Table S1. Selected bond lengths (Å) and angles (º) in complex **2**

Cu1–N1	1.957(2)
Cu1–N2	1.951(2)
N1–C1	1.294(3)
N2–C2	1.300(3)
C1–N3	1.336(3)
C2–N3	1.344(4)
C1–O1	1.366(3)
N1–Cu1–N2	88.39(9)
C1–N3–C2	119.2(2)
O1–C1–N1	115.1(2)