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Cu(II)-silsesquioxanes as efficient precatalysts for Chan-Evans-Lam coupling

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ABSTRACT

Two cage copper(II)silsesquioxanes, namely, tricopper complex $(\text{PhSiO}_{1.5})_8(\text{CuO})_3(\text{TMEDA})_2^*(\text{MeCN})_3$ **Cu-1** and hexacopper complex $(\text{MeSiO}_{1.5})_{12}(\text{CuO})_6(\text{Py})_6^*\text{TMEDA}$ **Cu-2** were synthesized (in 30% and 16% yield, respectively) via TMEDA-assisted reactions (TMEDA = tetramethylethylenediamine). Structural features of both products were established by X-ray diffraction study. Complexes **Cu-1** and **Cu-2**, along with some Cu(II)-silsesquioxanes reported earlier, were evaluated for the first time as precatalysts for the homogeneous Chan-Evans-Lam (CEL) O-arylation of benzoic acids (the highest yield of phenylbenzoic ester was 84%). Observed catalytic activity was superior to reference catalyst $\text{Cu}(\text{OAc})_2^*\text{H}_2\text{O}$. Finally, an application of copper-silsesquioxanes allowed to observe the first example of C-O CEL coupling under microwave activation characterized by (i) reduced loading of copper, (ii) low amount of added base, (iii) minimization of the time of reaction.

1. Introduction

The ability of copper ions to form cage complexes of various nuclearity [1–10] is extremely well known. In turn, high catalytic activity of copper complexes of different nuclearity is reported by many research teams. Among catalyzed reactions we could cite, e.g. selective oxidation of alkenes to carbonyls [11,12], oxidation of aliphatic and aromatic hydrocarbons [13–20], water oxidation [21,22], C–N and C–C couplings [23–25]. No less important process, namely, the oxidative coupling of nucleophiles with arylboronic acids (Chan-Evans-Lam (CEL) coupling), is also catalyzed by copper compounds. This reaction was firstly reported in 1998 [26–28] and since then many examples of simple copper salts'

application for CEL coupling were reported [29,30]. In turn, examples of MOF- [31–36], bi- [37,38] or polynuclear copper-based [39,40] catalysts remain scarce.

Encouraged by the recently reported high catalytic activity of polynuclear Cu(II)-cage complexes in oxidative hydrocarbons functionalization and amidation reactions [41–44], we were interested in the further investigations in this field. It is very likely that catalytic activity of compounds from refs. 41–44 is due to their heteroleptic nature. These complexes include sil- or germesquioxane fragments along with additional organic ligands, which could stabilize active species during catalytic act. Thus we have tried to obtain new representatives of this attractive family of metallacomplexes. Here we present our results regarding both the synthesis of heteroleptic (silsesquioxane/TMEDA) copper compounds and the first evaluation of metallasilsesquioxanes in catalysis of CEL.

2. Results and discussion

To take advantage of the presence of organic ligands

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coordinated to Cu-silsesquioxanes, we chose popular N-based ligand, namely TMEDA. Synthesis of Cu(II)-silsesquioxanes in the presence of TMEDA could lead to two types of cage-like products. First, in case of reaction starting from $\text{PhSi}(\text{OMe})_3$ (Scheme 1, left), formation of intriguing trinuclear compound $(\text{PhSiO}_{1.5})_8(\text{CuO})_3(\text{TMEDA})_2^+(\text{MeCN})_3$ **Cu-1** was observed. Complex **Cu-1** includes quite unusual, Si_8 -based fused bicyclic, siloxanolate ligand and two TMEDA fragments favoring the assembly of cage structure (Fig. 1). Compound **Cu-1** joins comparatively small family of trinuclear metallasilsesquioxanes [45–53]. In addition, molecular architecture of **Cu-1** is quite unlike to early reported structures of metallasilsesquioxanes bearing TMEDA ligands [54–56], which all belong to cubane-like type.

On the other hand, parallel reaction starting from $\text{MeSi}(\text{OMe})_3$ (Scheme 1, right) gives hexanuclear compound $(\text{MeSiO}_{1.5})_{12}(\text{CuO})_6(\text{Py})_6\text{TMEDA}$ **Cu-2** (Fig. 2). Product **Cu-2** represents more classical prismatic type of cage [57–63], characterized by ring-like location of metal ions. This type of molecular geometry has been early observed for both homoleptic [53,57–64] and heteroleptic (tris(2-pyridylmethyl)amine [65], tris(2-(dimethylamino)ethyl)amine [66] or 3,5-dimethylpyrazolate-containing [67]) metallasilsesquioxanes. Unlike in complex **Cu-1**, TMEDA does not coordinate the cage moiety of **Cu-2** and serves only as solvating ligand. Nevertheless, the presence of TMEDA in the reaction media doubtlessly influences the procedure of self-assembly of cage copper-silsesquioxane **Cu-2** in pyridine media. We could cite here recent reports by us [64] and Kononevich [68] describing copper-silsesquioxane synthesis in pyridine media without application of TMEDA. Both publications witnessed the formation of prismatic Cu_5 -silsesquioxanes instead of Cu_6 product **Cu-2**.

Significant difference in types of molecular architecture of products **Cu-1** and **Cu-2** persuaded us to illustrate self-assembly of **Cu-1-2** by using of DFT calculations. No doubt that governing role in both syntheses is played by ligand competition (MeCN vs TMEDA for **Cu-1**, Py vs TMEDA for **Cu-2**). A comparison of the enthalpy of protonation of the nitrogen atom in the three considered ligands was performed so to assess the N-donor ability of these agents. DFT [69] calculations (PBE/3z) show that the enthalpy of this process for

Fig. 1. Molecular structure of heteroleptic (TMEDA/silsesquioxane) copper(II) complex **Cu-1**. Color code: copper – green, silicon – yellow, oxygen – red, nitrogen – blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

TMEDA is 35.75 kcal/mol higher than the similar value for MeCN. As a result, TMEDA ligands succeeded in coordination of copper centers of arising complex **Cu-1**. Note that TMEDA species ligate two copper ions of **Cu-1**, making the third copper center spatially blocked (Fig. 3, top). In case of **Cu-2**, the calculations showed that the TMEDA protonation enthalpy exceeds the same value for Py by a very small amount (7.1 kcal/mol). This fact, along with an excess of Py in the reaction mixture, leads to governing role of pyridine ligands during self-assembly of **Cu-2**. Namely, pyridine species coordinate each copper ion of **Cu-2** (Fig. 3, bottom), while TMEDA is located outside the cage. It is noteworthy that due to spatial limitations (see VdW radii) only four pyridine molecules are located in the plane of copper Cu_6 belt, and the two other pyridines are shifted by 43° (shown by the arrows, Fig. 3, bottom).

Scheme 1. TMEDA-assisted synthesis of Cu(II)-phenylsilsesquioxanes **Cu-1** $(\text{PhSiO}_{1.5})_8(\text{CuO})_3(\text{TMEDA})_2^+(\text{MeCN})_3$ on the left and **Cu-2** $(\text{MeSiO}_{1.5})_{12}(\text{CuO})_6(\text{Py})_6\text{TMEDA}$, on the right).

Fig. 2. Top. Molecular structure of copper(II)silsesquioxane complex **Cu-2** with TMEDA as solvating ligand, front view. Bottom. Complex **Cu-2**, top view. Color code: copper – green, silicon – yellow, oxygen – red, nitrogen – blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2.1. Catalytic screening

In literature, TMEDA-containing copper complex $[\text{Cu}(\text{OH})(\text{TMEDA})]_2\text{Cl}_2$ was shown to catalyze: a) the coupling of arylboronic acids with imidazoles without extra additive of base [37]; b) the phosphorous–carbon bond formation–oxygenfunctionalization by interaction between phosphine-boranes and aryl-substituted alkynes [81] and c) the regioselective 2-arylation of 5-substituted tetrazoles with boronic acids [82]. Thus, compounds **Cu-1** and **Cu-2**, containing TMEDA ligands, were evaluated as precatalysts for Chan-Evans-Lam O-arylation of benzoic acids. To widen the scope of catalysts tested, copper silsesquioxanes **Cu-3** [72] (bearing oxidized 1,1-bis-(diphenylphosphino)methane, dppm, ligands) and **Cu-4** [73] (containing no additional organic ligands), reported by some of us earlier (Figs. 4 and 5), as well as simple copper salts, were examined (Table 1 and Table S1, see experimental section). Noteworthy, all previous reports on direct coupling of benzoic and boronic acids [70,71,74,75] suffer from certain limitations, e.g. high catalyst loadings (up to 40 mol % of copper source), significant reaction time (12–24 h), and excess of base (when necessary) [31,75]. In our case, benzoic acid **1a** and phenylboronic acid **2a** were reacted under microwave irradiation for 40 min, using *tert*-butylperoxide as a cheap oxidant and pyridine as base [71,76,77]. As it occurred to us that *tert*-butylperoxide and **2a** would degrade during the course of the reaction, both of the reagents were added portionwise (see

Fig. 3. Top. Simplified structure of **Cu-1**, representing Van der Waals radii. Center. Bottom. Simplified structure of **Cu-2**, representing Van der Waals radii and shift of two pyridine ligands from copper-containing ring.

experimental section). Reaction with 20 mol% of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and 3.5 eq. of pyridine allowed to reach full conversion (Table 1, entry 1). Reducing the quantity of **2a** and oxidant to 2.5 eq. revealed detrimental to the final yield (71%, entry 2). Attempts to reduce the catalyst loading and the quantity of base lowered the conversion to 58% (entry 3). On the other hand, with only a stoichiometric quantity of pyridine, complex **Cu-1** revealed high activity when 20 mol% of copper were used, yielding phenylbenzoic ester **3a** in 79% (entry 4). Reducing the loading to 15 mol% of copper gave 67% conversion, proving that **Cu-1** was more active than $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (entries 3 and 5). Since **Cu-2** already contains pyridine into its structure, it was evaluated without additional pyridine.

However, ester **3a** was isolated in only 30% yield (entry 6). Using complexes **Cu-3** and **Cu-4** with a loading of copper of 15 mol% gave desired ester **3a** in 84% and 22% yield, respectively (entries 7 and 8). Working at a loading of copper reduced to 10 mol% in the presence of **Cu-3**, the most active catalyst, gave a satisfactory conversion of 95% and an isolated yield of 80% (entry 9). It is important to note that optimization of the reaction conditions using microwave activation and copper(II) silsesquioxanes as precatalysts allowed one to successfully overcome the aforementioned issues in the CEL coupling, i.e. high catalyst loading, long reaction time and excess of base.

Complex **Cu-3** was then evaluated in the CEL coupling using different benzoic and boronic acids (Scheme 2). Utilizing 3,4-dimethoxybenzoic acid furnished corresponding ester **3b** in 74% yield. With electron-withdrawing groups, such as cyano and acetate, reaction was also found to be efficient, yielding **3c** and **3d** in

Fig. 4. Top. Molecular structure of copper(II)silsesquioxane complex **Cu-3** with dppmO₂ as solvating ligand, front view. Bottom. Complex **Cu-3**, top view. Color code: copper – green, silicon – yellow, oxygen – red, phosphorus – purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Molecular structure of copper(II)silsesquioxane complex **Cu-4**. Color code: copper – green, silicon – grey, oxygen – red, sodium – yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

68% and 81%, respectively. Using 4-bromobenzoic acid provided corresponding ester **3e** in 65% yield. Interestingly, despite of the strong reaction conditions (130 °C, (tBuO)₂), compound **3f**, which contains a sensitive furan ring, was obtained in 46% yield. Finally, replacing phenyl boronic acid with 3-chlorophenylboronic acid furnished corresponding ester **3g** in 40% yield.

According to previously reported mechanistic investigations on

CEL-reaction [78–80], the following mechanism of esterification of carboxylic acids using boronic acids is proposed (Scheme 3): at the first step (i) transmetalation of copper complex with boronic acid **2a** occurs to give intermediate **A**; then (ii) intermediate **A** is oxidized by another copper(II) complex to form Cu^{III}-containing intermediate **B**; at the third step (iii) C–O reductive elimination of **3a** to form Cu^I-intermediate **C** occurs, in turn to closing the catalytic cycle (iv) after oxidation of intermediate **C** by (tBuO)₂.

In order to compare this catalytic reaction with literature data, we calculated TON (turnover number) and TOF (turnover frequency) using previously reported results (Table 2). The Cu(OTf)₂-catalyzed reactions require either 40 mol% of catalyst, or 20 mol% if 2 equiv. of silver carbonate are added, to give TON values up to 2.4 and 3.5, and TOF values up to 0.2 and 1.8, respectively (entries 1 and 2). The Cu(OAc)₂·H₂O-catalyzed reaction shows better values of TON and TOF (entry 4), however, when using MOF Cu₃(BTC)₂ as catalyst TON values up to 6.1 are obtained (entry 5). **Cu-1** is slightly less efficient than regular copper acetate (entry 3). However, **Cu-3** gives the highest TON and TOF values in comparison to all previously used copper-containing catalysts (entry 6).

3. Conclusions

Two unusual cage copper(II)silsesquioxanes, (PhSiO_{1.5})₈(–CuO)₃(TMEDA)₂*(MeCN)₃ **Cu-1** and (MeSiO_{1.5})₁₂(CuO)₆(–Py)₆*TMEDA **Cu-2** were prepared via TMEDA-assisted self-assembly reactions from corresponding alkoxy silanes. Complexes **Cu-1** and **Cu-2** as well as other types of copper(II) silsesquioxanes (**Cu-3** and **Cu-4**) were evaluated for the first time in the Chan–Evans–Lam reaction. High efficiency of copper(II) silsesquioxanes, outmatching activity of simple copper salts, was revealed. Also, using of microwaves as an activation mode for such reactions was established. Further investigations, devoted to the study of heteroleptic metallasilsesquioxane complexes and their application in catalysis, are on their way in our teams now.

4. Experimental section

4.1. Chemicals

MeSi(OMe)₃, PhSi(OMe)₃ and TMEDA were purchased from Merck and used as received. All manipulations required no inert atmosphere.

4.2. Synthesis of complexes

Cu-1: 1.5 g (7.6 mmol) of PhSi(OMe)₃ was placed in a round-bottom flask (equipped with condenser and magnetic stirrer) and dissolved in 40 ml EtOH. Afterwards, 0.23 g (5.7 mmol) of NaOH was added and the mixture was heated at reflux for 2 h. Then, 0.38 g (2.8 mmol) of anhydrous CuCl₂ was added, reaction mixture was left stirring overnight and then filtered from NaCl. 0.22 g (1.9 mmol) of TMEDA in 35 ml of MeCN was added to the filtrate. In approximately 10 days the resulted solution gave crystalline material (0.46 g, 30% yield) appropriate for X-ray diffraction study (see below for details). Elemental analysis (XRF analysis, spectrometer VRA-30) calcd. (%) for C₆₆H₈₁Cu₃N₇O₁₅Si₈: Cu 48.70, Si 13.80, N 6.02; found Cu 48.58, Si 13.71, N 5.81.

Cu-2: 1.5 g (11.1 mmol) of MeSi(OMe)₃ was placed in a round-bottom flask (equipped with condenser and magnetic stirrer) and dissolved in 40 ml EtOH. Afterwards, 0.44 g (11.1 mmol) of NaOH was added and the mixture was heated at reflux for 2 h. Then, 0.75 g (5.6 mmol) of anhydrous CuCl₂ was added, reaction mixture was left stirring overnight and then filtered from NaCl. 0.30 g (0.027 mmol) of TMEDA in 35 ml of pyridine was added to the

Table 1
Screening the catalytic activity of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{II})$ -silsesquioxanes (**Cu 1–4**).^a

$\text{PhCO}_2\text{H} \quad \text{1a} + \quad \text{PhB(OH)}_2 \quad \text{2a} \xrightarrow[\text{MeCN, MW, 130 } ^\circ\text{C, 40 min}]{\text{Copper catalyst, pyridine, (tBuO)}_2} \text{PhCO}_2\text{Ph} \quad \text{3a}$				
Entry	Catalyst	Copper loading (mol %)	Equiv. of Py	Yield 3a % (Conv. %) ^{b,c}
1	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	20	3.5	84 (98)
2 ^d	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	20	3.5	71
3	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	15	1	(58)
4	Cu-1	20	1	79 (99)
5	Cu-1	15	1	(67)
6	Cu-2	15	—	30
7	Cu-3	15	1	84 (99)
8	Cu-3	10	1	80 (95)
9	Cu-4	15	1	22

^a Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), copper catalyst (10–20 mol %), $(\text{tBuO})_2$ (0.9 mmol) and pyridine in MeCN (3.0 mL), 130 °C, 40 min, MW.

^b Isolated yields are given in bold type. Conversion values are given in parenthesis.

^c Conversion was evaluated by HPLC analysis.

^d 0.75 mmol of **2a** and 0.75 mmol of $(\text{tBuO})_2$ were used.

Scheme 2. Screening of catalytic activity complex **Cu-3** with different substituted benzoic and boronic acids. The reported yields correspond to isolated solid products.

Scheme 3. Proposed mechanism of synthesis carboxylic esters.

Table 2
Comparison of TON and TOF with literature.

Entry	Catalyst	TON	TOF (h^{-1})	Reference
1	$\text{Cu}(\text{OTf})_2$	<2.4	<0.2	[70]
2	$\text{Cu}(\text{OTf})_2 + [\text{Ag}_2\text{CO}_3]$	<3.5	<1.8	[74]
3	Cu-1	<4	<6	This work
4	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	<4.2	<6.3	This work
5	$\text{Cu}_3(\text{BTC})_2$	<6.1	<0.6	[31]
6	Cu-3	<8	<12	This work

TON=(mmol of product)/(mmol of copper); TOF = TON/(reaction time); TON and TOF were calculated using literature data and according to definition of TON and TOF terms [19].

filtrate. In approximately two weeks the resulted solution gave crystalline material (0.28 g, 16% yield) appropriate for X-ray diffraction study (see below for details). Elemental analysis (XRF analysis, spectrometer VRA-30) calcd. (%) for $\text{C}_{48}\text{H}_{82}\text{Cu}_6\text{N}_8\text{O}_{24}\text{Si}_{12}$: Cu 20.35, Si 17.99, N 5.98; found Cu 20.11, Si 17.89, N 5.82.

4.3. Synthesis of carboxylic esters

General considerations: all reagents were purchased from Aldrich Chemical Co., Fluka, abcr Chemie Rus LLC, Alfa Aesar and used without further purification. Analyses were performed at the 'Plateforme Technologique Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier), at the INEOS RAS and at the Shared research and educational center of the Peoples' Friendship University of Russia (SREC PFUR, RUDN University). ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl_3 at 7.25 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on Bruker Avance III HD 100 MHz spectrometer and on Bruker Avance 400 (100 MHz). Chemical shifts are reported in ppm and referenced to the solvent peak (CDCl_3 at 77.00 ppm). The microwave irradiation experiments were carried out in a Monowave 400 reactor from Anton Paar GmbH and in a Biotage®Initiator+ microwave synthesizer. The reactions were carried out in 10 mL G10 glass tubes, sealed with silicon septum and placed in the microwave cavity. Analytical high performance liquid chromatography was performed on a Waters Millenium 717 that was equipped with an autosampler and had a variable wavelength

diode detector. A Chromolith RP18 column (50*4.6 mm) was employed, and a flow rate of 5 mL min⁻¹ was used with a linear gradient of CH₃CN in water of 0–100% (0.1% TFA) over 4.5 min.

General procedure: 0.3 mmol of corresponding aromatic carboxylic acid, 0.45 mmol of corresponding aromatic boronic acid, catalyst **Cu-3** (11 μmol, 32 mg), 0.3 mmol of Py and 0.45 mmol of (tBuO)₂ were dissolved in 3 mL of MeCN. The reaction was carried out 20 min at 130 °C in sealed vial in MW conditions. After the first step were added the new portion of 0.45 mmol of corresponding aromatic boronic acid and 0.45 mmol of (tBuO)₂ in the vial, and reaction was conducted at the same conditions as in a first step (sealed vial, 130 °C, 20 min). Solvent was then evaporated under vacuum and the obtained residue was purified by flash chromatography on silica gel to give corresponding carboxylic ester (**3a-g**).

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