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$Cu_{24}O_{24}Si_8R_8$: Organic Soluble 56-Membered Copper(I) Siloxane Cage and Its Use in Homogeneous Catalysis

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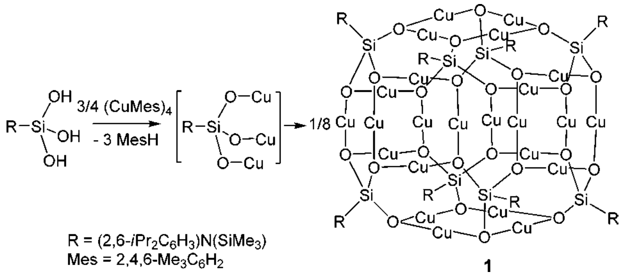
Abstract: Organic soluble 56-membered copper(I) siloxane cage compound $Cu_{24}O_{24}Si_8R_8$ (**1**, R = (2,6-$i$$Pr_2C_6H_3$)N($SiMe_3$)) has been synthesized and structurally characterized. It consists of a copper silica-supported structure, in which the metal ions are two-coordinate and covalently anchored onto the cage surface and the weak metal···metal $d^{10}-d^{10}$ interactions are widely full within the cage, that is active in catalyzing the Ullmann−Goldberg-type C−N coupling reaction involving aryl or 2-thienyl bromides with heterocyclic nitrogen nucleophiles. This work provides insight into homogeneous catalysis utilizing the heterogeneous structure.

Silica-supported copper-containing catalysts have been investigated for a number of reactions and are of industrial importance.[1] The activities and selectivities of these catalysts are usually affected by the size and shape of the metal particles dispersed on the silica surface as well as by the interaction between the metal and the silica.[2] However, these features still remain not easily controllable due to the heterogeneous nature of the catalysts normally prepared via ion-exchange procedures.[1,3] The X-ray single-crystal structural analysis of related species, such as $Na_2CuSi_4O_{10}$,[4a] $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$,[4b] $Na_2Cu_3Si_4O_{12}$,[4c] and $Na_4[Cu_2Si_{12}O_{27}(OH)_2][(AOH)_x(NaOH)_y(H_2O)_z]$ (A = Na, K, Rb, Cs, $x \approx 1$, $y \approx 1$, $z \approx 6$),[4d] reveals a variety of products either in composition or in structure. In recent years, the use of copper organosiloxy complexes as single-source precursors has been proven to be the method of choice for controlling at the molecular level the exact stoichiometry upon calcination to remove organic components.[5] These compounds can be synthesized with elimination of arene (or alcohol) when organosilanols and copper aryls (or alkoxides) are used as reactants. More importantly, such preparation may model the common mild support of the metal species on silica due to the SiOH groups present on the surface.[6] It has been shown that by using the triorganosilanol ligand tetrameric compounds $(CuOSiR'_3)_4$ (R'_3 = (OtBu)$_3$, Ph(OtBu)$_2$,[5b] Et_3, $Me_2$$t$Bu, Ph_3[7a]) are usually formed. However in the presence of donor ligands monomeric ($t$$Bu_3$P)$CuOSiPh_3$[7b] and dimeric $(LCuOSiR'_3)_2$ (R'_3 = Ph_3, L = PMe_2Ph; R'_3 = Ph_3, L = PEt_3; R'_3 = $Me_2$$t$Bu; L = PPh_3; R'_3 = (OtBu)$_3$, L = PPh_3)[7a] species are produced. This may reveal the self-assembling formation of the tetramer via the $CuOSiR'_3$ unit owing to the Lewis acidic Cu and the Lewis basic O atom, although isolated compounds of this composition are rare. Keeping in mind this assembly, we became interested in the approach of such a compound by using an organosilanetriol precursor. The organosilanetriol has been documented to assemble a variety of metallosiloxanes;[8] however, it has not been explored with copper species. Herein we report on the reaction of the organocopper(I) $(CuMes)_4$ (Mes = 2,4,6-$Me_3C_6H_2$)[9] with the N-bonded silanetriol $RSi(OH)_3$ (R = (2,6-$i$$Pr_2C_6H_3$)N($SiMe_3$)).[8c] A large cage compound $Cu_{24}O_{24}Si_8R_8$ (**1**, Scheme 1) was successfully isolated and characterized featuring a 56-membered CuSiO core with the copper(I) ions anchored on the cage surface. This is different from the other metallosiloxanes and represents, to the best of our knowledge, a new structural type.[8] Also, **1** was found to be catalytically active for the Ullmann−Goldberg-type C−N coupling reaction[10] involving aryl or 2-thienyl bromides and heterocyclic nitrogen nucleophiles.

Scheme 1. Synthesis of Compound **1**



The reaction of $(CuMes)_4$ with $RSi(OH)_3$ in a molar ratio of 0.75:1 proceeded in toluene from −10 °C to room temperature and afforded, after removal of all volatiles and subsequent extraction with n-hexane, light yellow crystals of **1** in good yield (75%). With elimination of MesH, $(CuO)_3SiR$ may be concomitantly formed. The single $CuOSiR'_3$ assembles into a tetramer.[5b,7a] The $(CuO)_3SiR$ may then three-dimensionally form an octamer constructing a large cage based on the well-defined tetrahedral geometry around the Si atom (see Supporting Information section IV (SI IV)).

1 is air-sensitive and changes the color to brown when exposed to air whether in the solid state or in solution, indicative of univalent copper in **1**. It can be stable up to 262 °C and, exceeding this temperature, turns brown and finally black. **1** is almost insoluble in n-hexane although crystallized from this solvent and sparingly soluble in aromatic solvents. However, it can smoothly be dissolved in CH_2Cl_2, $CHCl_3$, and THF. The ^1H NMR spectrum of **1** recorded in $CDCl_3$ exhibits two singlets (δ 0.06 and 0.08 ppm) that correspond to the $SiMe_3$ proton resonances as well as two doublets (δ 1.07 and 1.10 ppm) and one septet (δ 3.35 ppm) that correspond to the respective isopropyl methyl and methine proton resonances of the N-aryl substituents. The corresponding ^{29}Si NMR spectrum shows two resonances at δ −58.34 and 5.70 ppm. The latter is characteristic of the $SiMe_3$ group, and the former is assigned to the SiO_3 segment.

The composition of compound **1** was further confirmed by X-ray crystallography. The structural analysis reveals **1** as a large cluster

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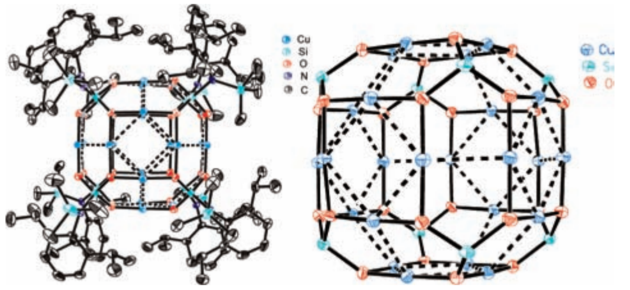

Figure 1. Crystal structure of **1** and its cage core at 50% thermal ellipsoid level.

compound (Figure 1) with the whole molecule composed of a regular polyhedron symmetrically surrounded by eight organic groups. The core contains 24 Cu, 8 Si, and 24 O atoms forming a 56-membered cage. These atoms constitute six square-planar Cu_4O_4 (the least-squares plane $\Delta = 0.0103-0.0411$ Å) and twelve hexagonal-planar $Cu_2Si_2O_4$ planes ($\Delta = 0.0224-0.0437$ Å), which are well-arranged to an octadecahedron (see SI IV).

In the core of **1**, all Cu atoms are two-coordinate with an almost linear geometry. The Cu−O bond lengths (1.831(4)−1.865(3) Å) and O−Cu−O angles (174.53(14)°−177.49(14)°) (see SI IV) are comparable to those found in the tetramers $(CuOSiPh_3)_4$ (Cu−O, 1.833(4)−1.856(4) Å; O−Cu−O, 175.35(17)°−176.32(17)°)[7a] and {Cu[OSiPh(O*t*Bu)$_2$]}$_4$ (1.827(5)−1.844(4) Å; 174.1(2)°−174.3(2)°).[5b] All O atoms are three-coordinate and are connected by one Si and two Cu atoms with the peripheral angle of each O atom in the range 336.98(16)°−350.70(16)°. These angles vary strongly when compared to those for the Si atom in the SiO_3 segment (328.50(16)°−328.65(16)°). This indicates that the coordination geometry around the Si atom plays a prominent role in constructing the cage structure of **1**. It is quite interesting that within the cage framework the Cu···Cu separations are in the range from 2.6296(8) to 2.7204(8) Å. The $d^{10}-d^{10}$ interactions have been discussed as being attractive among the multinuclear Cu(I) complexes considering the remarkably short Cu···Cu distance.[11] This might be a general tendency to form a cluster by such interactions.

Table 1. Coupling of Aryl or 2-Thioenyl Bromides with Imidazol or Pyrazole Using **1** as Catalyst[a]

Run	Ar−Br	HN-cycle	Conditions °C/h	Solvent	Yield[b]
1	phenyl bromide	imidazole	110, 24	DMF	92%
2	phenyl bromide	pyrazole	80, 12	CH_3CN	93%
3	phenyl bromide	3,5-dimethylpyrazole	80, 24	CH_3CN	43%
4	*p*-tolyl bromide	imidazole	110, 24	DMF	81%
5	*p*-tolyl bromide	pyrazole	80, 12	CH_3CN	87%
6	*p*-tolyl bromide	3,5-dimethylpyrazole	80, 24	CH_3CN	43%
7	mesityl bromide	imidazole	110, 24	DMF	22%
8	mesityl bromide	pyrazole	80, 12	CH_3CN	trace
9	mesityl bromide	3,5-dimethylpyrazole	80, 24	CH_3CN	trace
10	2-thienyl bromide	imidazole	110, 24	DMF	86%
11	2-thienyl bromide	pyrazole	80, 12	CH_3CN	90%
12	2-thienyl bromide	3,5-dimethylpyrazole	80, 24	CH_3CN	45%

[a] Ar−Br (1.5 mmol), HN-cycle (2.25 mmol), **1** (5.8 μmol), Cs_2CO_3 (3 mmol), solvent (3 mL). [b] Isolated yield; the products were confirmed by ^1H and ^{13}C NMR spectral analysis (see SI V).

The use of **1** as a catalyst for investigating the Ullmann−Goldberg-type C−N coupling reaction has been accomplished utilizing aryl or 2-thienyl bromides and heterocyclic nitrogen nucleophiles. The results are shown in Table 1. With a loading of 0.39 mol % **1** and the use of Cs_2CO_3 as base, an initial reaction was conducted between PhBr and an excess of imidazole in DMF at 110 °C for 24 h, providing the *N*-phenyl-imidazole product reproducible in a yield of 92%. This yield can be compared with that of the ligand-free CuI (20 mol %) reacted under similar conditions for a longer period of time (40 h) (91% yield),[12a] whereas a lower yield (43%) is obtained for CuI (10 mol %) using CH_3CN as solvent at 82 °C in the presence of 20 mol % phenolic-type ligand (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one.[12b] An alteration of the aryl bromide to *p*-tolyl bromide yielded *N*-*p*-tolyl-imidazole in 81% yield; however, the use of mesityl bromide lowers the yield of *N*-mesityl-imidazole to 22%. This suggests an influence of the functionalities at the phenyl ring in the C−N coupling reaction, as has been discussed in terms of the steric and electronic properties of the functionalities. Encouraged by these results, we explored the catalytic reactions further by changing the aryl bromide to 2-thienyl bromide or the nitrogen nucleophile to pyrazoles. The catalytic results are comparable to those reported for other catalyst systems.[13]

It is generally considered that the copper ion in the catalytic Ullmann−Goldberg-type C−N coupling reaction should be monovalent.[14] Thus, it is reasonable for the Cu(I) center to undergo the oxidative reaction of the aryl bromide to a form Cu(III) intermediate followed by the C−N coupling reaction in the presence of the nitrogen nucleophile,[15] although in some cases CuO or Cu(II) apatite was found to be catalytically active, which could involve a change of the copper oxidation state during the reaction process.[16] To date, for this catalytic reaction, simple copper salts, copper oxides, or copper metal in the presence or absence of ancillary ligands have been studied.[12−16] However compound **1** as a copper(I) siloxane has proven to be an equal or superior catalyst in this family. Moreover, **1** is soluble in organic solvents but has a clear silica-supported structure. This work provides insight into homogeneous catalysis utilizing the heterogeneous structure. Investigation into the details of the catalytic interactions and the use of this compound for other catalytic reactions is in progress.

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Supporting Information Available: Experimental Section including detailed synthetic procedures, analytical and characterization data, and CIF data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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