

# A recyclable nanosize aminoarenethiolato copper(I) catalyst for C–C coupling reactions

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## Abstract

An aminoarenethiolato copper(I) catalyst was attached to a carbosilane dendritic wedge, which had been prepared via a novel convergent synthetic method. Compared with the unsupported complex, this novel dendritic copper(I) catalyst is more robust towards hydrolysis and oxidation and has increased solubility in common organic solvents. The catalytic activity of the dendritic copper catalyst was tested in the 1,4-addition of  $\text{Et}_2\text{Zn}$  to 2-cyclohexenone. In both polar ( $\text{Et}_2\text{O}$ ) and apolar (hexane) solvents excellent activity was observed. The fact that the catalytic copper site remains attached to the nanosize dendritic aminoarenethiolate ligand allows separation of this catalyst by means of nanofiltration.

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## 1. Introduction

Continuous recycling of soluble transition-metal catalysts in homogenous catalysis is possible by application of catalysts immobilized on nanosize organic supports (e.g. carbosilanes [1,2] or cartwheel-type molecules [3]) in a membrane reactor [4]. These catalysts must have a stable metal–ligand bond otherwise leaching of the metal will rapidly reduce the performance and recyclability of the catalytic system. In copper-catalyzed reactions this prerequisite is difficult to fulfill [5], because only a few isolated cases are known in which the copper–ligand bond remains intact throughout the catalytic cycle. One of these cases involves the use of monoanionic aminoarenethiolato ligands which are *N,S*-bonded to copper(I) in a bidentate fashion. In particular the catalytic activity of aminoarenethiolato copper(I) **1a** has been extensively

studied, which appeared to have wide applicability as stable catalysts in, e.g. 1,4-additions [6–9], 1,6-additions [10] and allylic substitutions [11,12]. Although it is not the most active copper catalyst reported to date, recent studies showed that these aminoarenethiolato copper(I) catalysts are very robust, i.e. thermally stable and have considerable stability towards oxidation by air. Furthermore, mechanistic studies established that the covalent thiolato–copper bond is maintained throughout the catalytic cycle in processes involving the use of  $\text{RLi}$  [13],  $\text{RMgX}$  [6] and  $\text{R}_2\text{Zn}$  reagents [14]. A recent example, shown in Fig. 1, is the successful use of **1a** and **1b** as catalyst in the 1,4-addition of  $\text{Et}_2\text{Zn}$  to 2-cyclohexenone.

In contrast to the general low solubility of copper(I) salts as a consequence of their polymeric nature, the thiolato copper complexes, of type **1**, are well-defined aggregated species, usually trimers [15,16], and have favorable solubility properties, which can even be enhanced by the introduction of silyl groups (**1b**). Here we report the synthesis and catalytic properties of an aminoaren-

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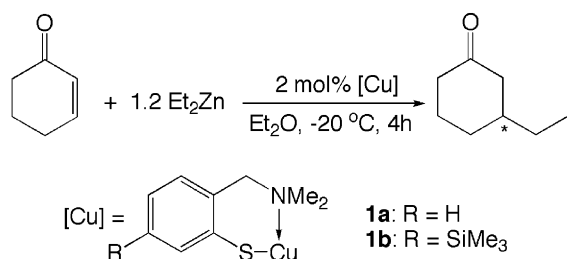


Fig. 1. 1,4-Addition of  $\text{Et}_2\text{Zn}$  to 2-cyclohexenone using copper(I) complexes **1a** and **1b** as catalysts.

ethiolato copper(I) catalyst that has been connected to the focal point of a dendritic wedge. This species exists in the resting state at least as a trimer which has a nanosize dimension. Consequently, this copper(I) catalyst can be separated from products and reagents and isolated by nanofiltration and subsequently reused.

## 2. Experimental

### 2.1. Chemicals and equipment

All experiments were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were carefully dried and distilled prior to use. Standard chemicals were purchased from Acros Organics or Aldrich, except for dimethylphenylsilane (Lancaster) and trivinylchlorosilane (ABCRC). 4-[(Dimethylamino)methyl]bromobenzene (**4**) was prepared according to a previously reported procedure [17–19].  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of all compounds were recorded in benzene- $d_6$  on a 300 MHz spectrometer at 298 K unless stated otherwise. GC measurements were carried out using a DB17 (30 m  $\times$  0.32 mm) column and GC-MS measurements were carried out on a Turbo Mass spectrometer. Fast Atom Bombardment (FAB) mass spectrometry was carried out on a four-sector mass spectrometer. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with Xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10,000 (10% valley definition) was used. MALDI-TOF mass spectrometry measurements were carried out on a mass spectrometer equipped with a nitrogen laser emitting at 337 nm. External calibration was performed using  $\text{C}_{60}$  and  $\text{C}_{70}$ . Sample and matrix (2,5-dihydroxybenzoic acid) solutions were prepared with an approximate concentration of 30 mg/mL in THF. A 0.2  $\mu\text{L}$  sample of the solution and 0.2  $\mu\text{L}$  of the matrix solution were combined and placed on the golden MALDI target and analyzed after evaporation of the solvents. Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium, Mühlheim/Ruhr, Germany.

### 2.2. Preparation of compounds 5–10

#### 2.2.1. Tris[2-(dimethylphenylsilyl)ethyl]chlorosilane (**5**)

Solid  $[(\text{Bu}_4\text{N})_2\text{PtCl}_6]$  catalyst (1 mg) was added to a solution of trivinylsilyl chloride (1.0 mL, 6.46 mmol) and dimethylphenylsilane (3.3 mL, 21.31 mmol) in THF (4 mL). The suspension was heated for 10 min in an oil bath at 80 °C and then the mixture was stirred overnight at room temperature. All volatiles were removed in vacuo yielding a crude yellowish viscous oil (3.45 g, 6.24 mmol, 96%) which was used without further purification.  $^1\text{H}$  NMR:  $\delta$  0.18 (s, 18H,  $3 \times \text{SiMe}_2$ ), 0.66–0.77 (m, 12H,  $3 \times \text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 7.20 (m, 9H,  $\text{ArH}(3,4,5)$ ), 7.42 (m, 6H,  $\text{ArH}(2,6)$ ).  $^{13}\text{C}$  NMR:  $\delta$  -3.53 ( $3 \times \text{SiMe}_2$ ), 7.81 ( $3 \times \text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 128.2 ( $\text{ArC}(2,6)$ ), 129.3 ( $\text{ArC}(4)$ ), 134.0 ( $\text{ArC}(3,5)$ ), 138.8 ( $\text{ArC}(1)$ ).  $^{29}\text{Si}$  NMR:  $\delta$  -12.24 ( $3 \times \text{SiMe}_2$ ), 24.51 ( $\text{SiCl}$ ).

#### 2.2.2. {Tris[2-(dimethylphenylsilyl)ethyl]}{4-[(dimethylaminomethyl)phenyl]}silane (**7**)

*t*-BuLi (7.5 mL, 11.2 mmol) was added to a solution of **4** (1.06 g, 4.96 mmol) in diethyl ether (17 mL) at -78 °C. After 30 min. a solution of **5** (2.88 g, 5.22 mmol) in diethyl ether (5 mL) was added to the cold mixture. After 25 min. the cloudy mixture was allowed to reach room temperature, stirred for another 18 h and subsequently quenched with  $\text{H}_2\text{O}$  (20 mL). The organic layer was separated and the aqueous layer was extracted with pentane ( $4 \times 10$  mL). The combined organic layers were dried on  $\text{Na}_2\text{SO}_4$  and filtered. All volatiles were removed in vacuo which yielded the pure yellow-colored viscous oil (2.50 g, 3.85 mmol, 77%).  $^1\text{H}$  NMR:  $\delta$  0.23 (s, 18H,  $3 \times \text{SiMe}_2$ ), 0.69–0.73 (m, 6H,  $3 \times \text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 0.83–0.87 (m, 6H,  $3 \times \text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 2.07 (s, 6H,  $\text{NMe}_2$ ), 3.27 (s, 2H,  $\text{CH}_2$ ), 7.21–7.23 (m, 9H,  $\text{SiMe}_2\text{ArH}(3,4,5)$ ), 7.39 (d, 2H,  $^3J = 7.5$  Hz,  $\text{SiArH}$ ), 7.44–7.49 (m, 8H,  $\text{SiMe}_2\text{ArH}(2,6)$  and  $\text{SiArH}$ ).  $^{13}\text{C}$  NMR:  $\delta$  -3.56 ( $3 \times \text{SiMe}_2$ ), 3.55 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ), 7.92 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ), 45.36 ( $\text{NMe}_2$ ), 64.40 ( $\text{CH}_2\text{N}$ ), 128.0 ( $\text{SiMe}_2\text{ArC}$ ), 128.6 ( $\text{SiArC}$ ), 129.0, 133.9 ( $\text{SiMe}_2\text{ArC}$ ), 134.6, 135.4 ( $\text{SiArC}$ ), 139.1 ( $\text{SiMe}_2\text{ArC}$ ), 140.6 ( $\text{SiArC}$ ).  $^{29}\text{Si}$  NMR:  $\delta$  -12.42 ( $3 \times \text{SiMe}_2$ ), -7.70 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ). MS (MALDI-TOF):  $m/z$  650.03 ( $[\text{M} + \text{DHB}]^+$ ) (calcd. 651.36). Anal. Calc. for  $\text{C}_{39}\text{H}_{57}\text{NSi}_4$ : C, 71.82; H, 8.81; N, 2.15; Si, 17.22. Found: C, 71.96; H, 8.86; N, 2.07; Si, 17.11%.

#### 2.2.3. {Tris[2-(dimethylphenylsilyl)ethyl]}{4-[(dimethylaminomethyl)-2-(trimethylsilylthio)phenyl]}silane (**8**)

*t*-BuLi (4 mL, 6.0 mmol, 1.5 M in pentane) was added to a solution of **7** (1.94 g, 2.98 mmol) in pentane (40 mL) at -78 °C. After 1 h, the orange solution was allowed to reach room temperature and was stirred for 2.5 days. The solution was concentrated to 20 mL in vacuo. Subsequently, cold THF (100 mL, 60 °C) was added and the solution was further cooled to -78 °C. Sublimed sulfur (0.19 g, 6.0 mmol) was added to the solution and the

reaction was stirred at low temperature. After 7 h, the reaction mixture was allowed to reach room temperature and was stirred overnight. Trimethylchlorosilane (1 mL, 7.88 mmol) was added and the solution was stirred for 4.5 h. All volatiles were removed in vacuo and toluene (50 mL) was added to the milky orange-colored viscous oil. After centrifugation the supernatant was separated and all volatiles were removed in vacuo which yielded a red-brown-colored oil (1.53 g, 2.03 mmol, 68%).  $^1\text{H}$  NMR:  $\delta$  0.22 (s, 9H,  $\text{SSiMe}_3$ ), 0.23 (s, 18H,  $3\times\text{SiMe}_2$ ), 0.66–0.75 (m, 6H,  $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 0.78–0.89 (m, 6H,  $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 2.19 (s, 6H,  $\text{NMe}_2$ ), 3.76 (s, 2H,  $\text{CH}_2\text{N}$ ), 7.16–7.26 (m, 9H,  $\text{SiMe}_2\text{ArH}(3,4,5)$ ), 7.38/7.70 ((AB, 2H,  $\text{SiArH}(3,4)$ ),  $J_{\text{AB}} = 7.6$  Hz), 7.44–7.53 (m, 6H,  $\text{SiMe}_2\text{ArH}(2,6)$ ), 7.84 (s, 1H,  $\text{SiArH}(6)$ ).  $^{13}\text{C}$  NMR:  $\delta$  -2.99 ( $3\times\text{SiMe}_2$ ), 1.76 ( $\text{SSiMe}_3$ ), 3.96 ( $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 8.25 ( $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 46.01 ( $\text{NMe}_2$ ), 62.97 ( $\text{CH}_2\text{N}$ ), 128.5, 129.5 ( $\text{SiMe}_2\text{ArC}$ ), 130.1, 131.9, 133.7 ( $\text{SiArC}$ ), 134.3, 139.5 ( $\text{SiMe}_2\text{ArC}$ ), 139.0, 143.0, 144.3 ( $\text{SiArC}$ ).  $^{29}\text{Si}$  NMR:  $\delta$  -12.43 ( $3\times\text{SiMe}_2$ ), -7.30 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ), -0.84 ( $\text{SSiMe}_3$ ). Anal. Calc. for  $\text{C}_{42}\text{H}_{65}\text{NSSi}_5$ : C, 66.38; H, 8.57; N, 1.79; Si, 18.48. Found: C, 66.69; H, 8.66; N, 1.85; Si, 18.56%.

#### 2.2.4. *{Tris[2-(dimethylphenylsilyl)ethyl]}{[4-(dimethylaminomethyl)-2-(copperthiolato)phenyl]}silane (9)*

A solution of **8** (1.49 g, 1.97 mmol) in toluene (20 mL) was added to a  $\text{CuCl}$  suspension (0.18 g, 1.87 mmol) in toluene (10 mL). The brownish suspension was stirred until all  $\text{CuCl}$  had reacted (1 h). All volatiles were removed in vacuo which yielded the crude red-brown-colored viscous oil (1.34 g, 1.80 mmol, 96%) which was purified by membrane filtration.  $^1\text{H}$  NMR (toluene- $d_6$ , 358 K):  $\delta$  0.21, 0.30 ( $2\times\text{s}$ , 18H,  $3\times\text{SiMe}_2$ ), 0.67–0.83 (m, 6H,  $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 0.86–0.99 (m, 6H,  $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 2.03–2.20 (m, 6H,  $\text{NMe}_2$ ), 3.31–3.82 (m, 2H,  $\text{CH}_2$ ), 6.78/7.14 ((AB, 2H,  $\text{SiArH}(3,4)$ ),  $J_{\text{AB}} = 7.6$  Hz), 7.20–7.25 (m, 9H,  $\text{SiMe}_2\text{ArH}(3,4,5)$ ), 7.47–7.50 (m, 6H,  $\text{SiMe}_2\text{ArH}(2,6)$ ), 8.12 (s, 1H,  $\text{SiArH}(6)$ ).  $^{13}\text{C}$  NMR (toluene- $d_8$ , 358 K):  $\delta$  -3.95 ( $3\times\text{Si}(\text{CH}_3)_2$ ), 3.70 ( $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 8.40 ( $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 47.79 ( $\text{NMe}_2$ ), 66.89 ( $\text{CH}_2\text{N}$ ), 127.8, 128.7 ( $\text{Si}(\text{CH}_3)_2\text{ArC}$ ), 129.6, 131.7, ( $\text{SiArC}$ ), 133.5, 133.6 ( $\text{Si}(\text{CH}_3)_2\text{ArC}$ ), 134.3, 138.9, 139.2 ( $\text{SiArC}$ ).  $^{29}\text{Si}$  NMR (toluene- $d_8$ , 358 K):  $\delta$  -12.50 ( $3\times\text{SiMe}_2$ ), -8.06 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ). MALDI-TOF-MS:  $m/z$  1558 ( $[\text{Cu}_3(\text{SAr})_2]^+$ ), 1492 ( $[\text{Cu}_2(\text{SAr})_2]^+$ ), 808 ( $[\text{Cu}_2(\text{SAr})]^+$ ), 745 ( $[\text{Cu}(\text{SAr})]^+$ ). FAB-MS: Rel. Peak Int.  $m/z$  1491 ( $[\text{Cu}_2(\text{SAr})_2]^+$ , 0.7%), 808 ( $[\text{Cu}_2(\text{SAr})]^+$ , 10%), 745 ( $[\text{Cu}(\text{SAr})]^+$ , 8%). Anal. Calc. for  $\text{C}_{39}\text{H}_{56}\text{CuNSSi}_4$ : C, 62.72; H, 7.56; N, 1.88. Found: C, 61.83; H, 8.03; N, 1.48%.

#### 2.2.5. *Tris-[2-(dimethylphenylsilyl)ethyl]silane (10)*

An ice-cooled solution of **5** (2.73 g, 4.94 mmol) in diethyl ether (10.5 mL) was added to  $\text{LiAlH}_4$  (93.7 mg, 2.47 mmol) in diethyl ether (7.5 mL). The grayish mixture

was stirred overnight at room temperature. After filtration through Celite, the colorless filtrate was added to  $\text{HCl}(\text{aq})$  (100 mL, 2 M). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  ( $2\times 100$  mL) and the combined organic layers were washed with  $\text{H}_2\text{O}$  ( $2\times 50$  mL) and with brine (100 mL). The mixture was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered through a pad of silica gel. The solvents were removed in vacuo which yielded a white milky oil (1.31 g, 2.52 mmol, 51%).  $^1\text{H}$  NMR:  $\delta$  0.20 (s, 18H,  $3\times\text{SiMe}_2$ ), 0.46–0.54 (m, 6H,  $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ), 0.58–0.66 (m, 6H,  $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})_3$ ), 7.13–7.22 (m, 9H,  $\text{ArH}$ ), 7.41–7.47 (m, 6H,  $\text{ArH}$ ).  $^{13}\text{C}$  NMR:  $\delta$  -2.98 ( $3\times\text{SiMe}_2$ ), 7.01 ( $\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 8.10 ( $3\times\text{Si}(\text{CH}_2\text{CH}_2\text{Si})$ ), 128.5 ( $\text{ArC}(2,6)$ ), 129.5 ( $\text{ArC}(4)$ ), 134.3 ( $\text{ArC}(3,5)$ ), 139.6 ( $\text{ArC}(1)$ ).  $^{29}\text{Si}$  NMR:  $\delta$  -12.39 ( $3\times\text{SiMe}_2$ ), -2.56 ( $\text{SiH}$ ). Anal. Calc. for  $\text{C}_{30}\text{H}_{46}\text{Si}_4$ : C, 69.42; H, 8.93; Si, 21.64. Found: C, 69.28; H, 9.06; Si, 21.61%.

#### 2.3. Membrane filtration

Crude **9** was dissolved in diethyl ether (10 mL) and transferred into a dialysis tubing under a purge of nitrogen. The dialysis tubing was sealed and placed in a closed system with diethyl ether (200 mL) under nitrogen. After stirring for 4 h the contents of the dialysis tube was transferred to a Schlenk flask and all volatiles were removed in vacuo.

#### 2.4. General procedure for 1,4-addition of diethylzinc to 2-cyclohexenone

The catalyst (20  $\mu\text{mol}$ ) was dissolved in dry solvent (2 mL) and cooled to  $-20$  °C. After 20 min,  $\text{Et}_2\text{Zn}$  (1.0 M solution in pentane, 1.2 mL, 1.2 mmol) was added. The mixture was stirred for 5 min and then 2-cyclohexenone (96  $\mu\text{L}$ , 1.0 mmol) was added. After 4 h the reaction mixture was quenched with 1 M  $\text{HCl}$  and the layers were separated. The organic layer was filtered through silica and reaction products were analyzed by GC.

#### 2.5. Molecular modeling

Molecular modeling was performed using SPARTAN 5.1.1 running on a SGI-O2 computer and calculations employed the MMFF84 forcefield. Parameters from the crystal structure of **1a** were used as the starting point for the aminoarenethiolato  $\text{Cu}(\text{I})$  portion of the molecule. Solvent effects were excluded in the calculations.

### 3. Results and discussion

In an explorative study, we began with linking a number of aminoarenethiolato copper(I) units to the

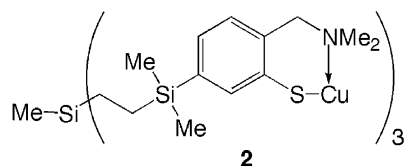


Fig. 2. A  $G_0$ -carbosilane dendritic species with peripheral aminoarene-thiolato copper(I) units.

periphery of a small carbosilane dendrimer (Fig. 2). Three aminoarene-thiolato copper(I) units were attached via the 5-arene position to the peripheral Si-groups of a  $G_0$ -dendritic wedge with the expectation that the three aminoarene-thiolato copper(I) units in **2** would trigger the formation of a trimeric aggregate by intramolecular S–Cu coordination. This assumption was based on the fact that the parent aminoarene-thiolato copper(I) compound exists both in the solid state and in solution as a trimeric aggregate [16], see Fig. 3. However, irrespective the method of preparation of **2**, a highly insoluble material was obtained, indicating that, instead of intramolecular aggregation, polymeric networks were formed as a result of intermolecular S–Cu bond formation.

To avoid the formation of such (insoluble) polymer networks and to obtain a soluble catalyst the strategy was changed and a single aminoarene-thiolato copper(I) unit was linked to the focal point of a carbosilane dendritic wedge. The choice of carbosilane dendritic materials as support in these studies is based on its chemical inertness which makes this material compatible with the harsh reaction conditions involved in both catalyst

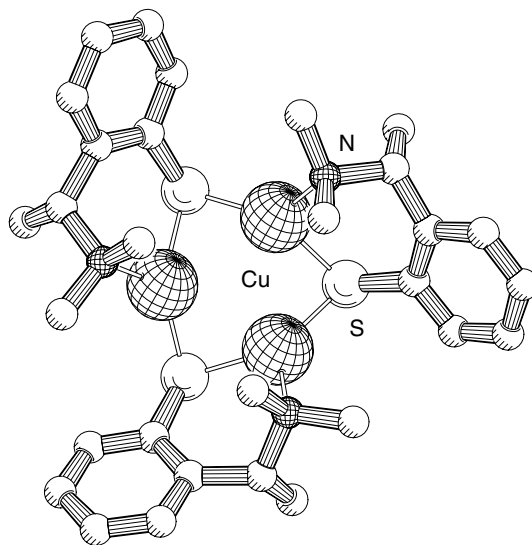
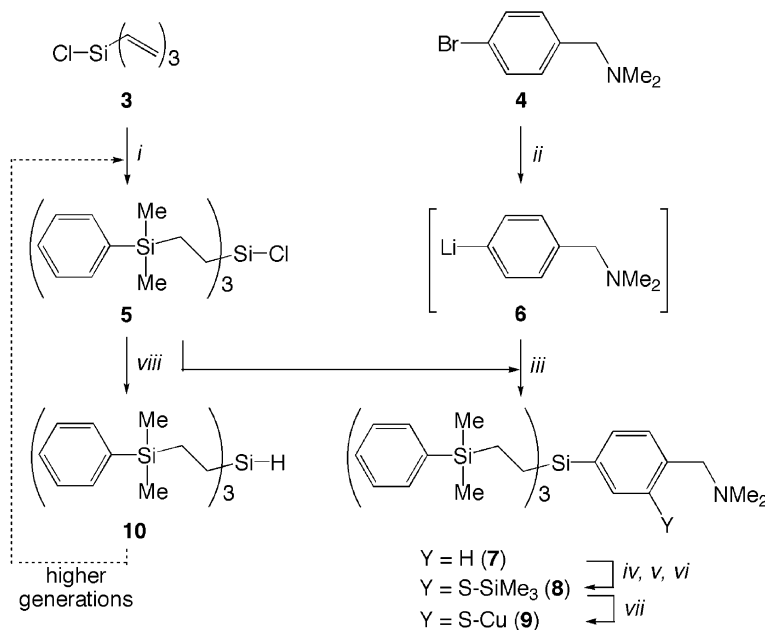


Fig. 3. X-ray structure [16] of the enantiopure  $\alpha$ -methyl-substituted analog of **1a**.

preparation and catalytic C–C coupling reactions with organometallic reagents [15–19].

$G_0$ -wedge **5** was prepared via a hydrosilylation reaction of trivinylchlorosilane (**3**) with 3.3 equivalents of dimethylphenylsilane (Scheme 1). Excess dimethylphenylsilane could be removed in vacuo. 4-[(Dimethylamino)methyl]-1-bromobenzene (**4**) was converted into the corresponding lithium derivative (**6**) and subsequently coupled to carbosilane wedge **5** to afford **7** [20].



Scheme 1. Reagents and conditions: (i) 3.3 eq. HSiMe<sub>2</sub>Ph, (Bu<sub>4</sub>N)<sub>2</sub>PtCl<sub>6</sub>, THF, 10 min, 80 °C; (ii) 2.2 eq. *t*-BuLi, Et<sub>2</sub>O, rt; (iii) Et<sub>2</sub>O, rt; (iv) 2 eq. *t*-BuLi, pentane, rt; (v) 1/4 S<sub>8</sub>, THF, –60 °C; (vi) excess SiMe<sub>3</sub>Cl; (vii) 0.95 eq. CuCl, toluene, rt; and (viii) LiAlH<sub>4</sub>, Et<sub>2</sub>O, rt.

Lithiation of **7** was accomplished by the addition of a twofold excess of lithiating reagent, *t*-BuLi, to ensure complete lithiation at the position *ortho* to the amino substituent [21]. A stoichiometric amount of sulfur relative to *t*-BuLi was used for the subsequent sulfur insertion reaction. The resulting lithium thiolate intermediate was quenched with trimethylsilyl chloride affording **8**. The *t*-butyl thioether formed as byproduct could be easily removed in vacuo. Reaction of the aryl trimethylsilyl thioether **8** with 0.95 equivalents of CuCl gave the desired aminoarenethiolato copper(I) complex **9**, as well as Me<sub>3</sub>SiCl, which was removed in vacuo (Scheme 1). Unreacted **8** was removed from **9** by passive dialysis [22] in diethyl ether (see Section 2). Complex **9** was isolated as a reddish oil and is soluble in common organic solvents ranging from tetrahydrofuran to hexane. FAB-MS and MALDI-TOF-MS spectra of **9** showed a peak at  $m/z = 745$  ([monomeric **9**]<sup>+</sup>, 8%), as well as peaks at 808 ([monomeric **9** + Cu]<sup>+</sup>, 10%) and 1491 ([dimeric **9**]<sup>+</sup>, 0.7%). The resonances found in the <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra of **9** confirmed its synthesis.

Most likely **9** has an aggregated structure like the parent compounds **1a** and **1b**. These parent compounds exist in benzene solution as trimeric aggregates comprising a six-membered Cu<sub>3</sub>S<sub>3</sub> ring in a chair configuration with alternating copper and sulfur atoms, see Fig. 3. Each sulfur atom bridges two copper atoms with all arene substituents taking equatorial positions [15,16]. Analysis of models of **2** indicate that, for intramolecular aggregation, all the arene substituents would occupy axial positions. Due to steric considerations, this configuration is disfavoured and intermolecular bonding is observed resulting in formation of polymeric insoluble products. However, the similar spectroscopic data of **9** and **1** with respect to the central Cu<sub>3</sub>S<sub>3</sub>-core would suggest a trinuclear structure ( $m/z = 2235$  g mol<sup>-1</sup>) for **9**.

The proposed aggregation of a number of monomeric units **9** is also in line with the successful purification of **9** from low molecular-weight impurities by using a passive membrane filtration of crude **9**. The membrane used separates molecules with a mass below 1200 Da from those with a mass above 2000 Da [23]. Since monomeric **8** has

a molecular mass of 745 g mol<sup>-1</sup>, separation from, for example **8**, can only occur when monomeric **9** has aggregated at least to trimers (molecular mass of 2235 g mol<sup>-1</sup>) [24–27].

Molecular mechanics calculations [28] were carried out to gain more insight in the size and shape of the molecular structure of **9** (Figs. 4 and 5). The structures of both monomeric and trimeric **9** have been calculated and both showed a relatively flat structure. They have average diameters of 1.6 and 2.3 nm, and molecular volumes of 869 and 2583 Å<sup>3</sup>, respectively (Figs. 4 and 5) [28].

Complex **9** was tested as a catalyst in the 1,4-addition reaction of diethylzinc to 2-cyclohexenone in a variety of solvents (Fig. 1). The results were compared to those obtained with unsupported complexes **1a** and **1b**. The catalytic performance of metallodendrimer **9** (entries 6–10) is similar to those of unsupported copper(I) complexes **1a** and **1b** (entries 2 and 5) or even exceeds these (compare entries 3 and 4 with entries 7 and 8) (Table 1). The influence of *para*-substitution had already been studied with catalyst **1b** (entry 5) [14].

The increase in activity in toluene and THF going from **1a** to **9** indicates that the presence of the wedge has a positive influence on the catalytic activity. This is most likely due to the improved physical properties of **9**, i.e. solubility, and better stability to hydrolysis and oxidation. The improved solubility of **9** prompted us to perform the same catalysis in less common solvents for these reactions, such as hexane and dichloromethane (entries 9 and 10). Interestingly, the activity and selectivity of the dendritic catalyst in hexane were similar to those in the other more polar solvents, except THF.

After quenching of the reaction mixture with aqueous HCl (entry 6), the organic layer was submitted to nanofiltration in order to recover **9** as a solution in Et<sub>2</sub>O. The fraction retained by the membrane was subjected to another catalytic run and the 1,4-addition product was formed quantitatively, proving the presence of active catalyst after recycling. The stability of catalyst **9** in solution towards repeated exposure to water demonstrates its robustness as compared to **1a**. Moreover, exposure of a solution of **1a** to air results in rapid

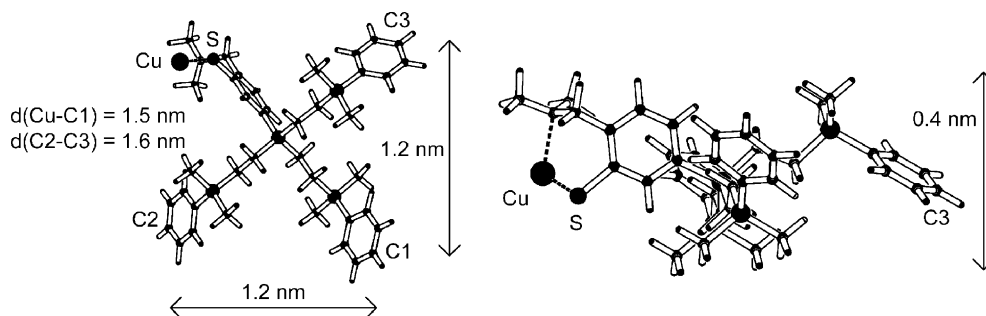


Fig. 4. Molecular modeling of monomeric **9**; topview and sideview.

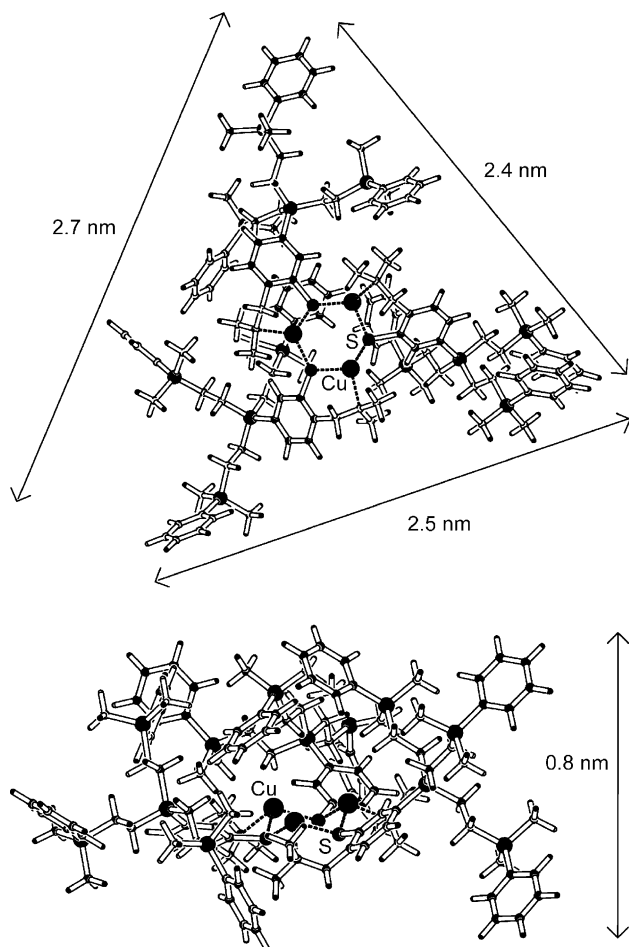


Fig. 5. Molecular modeling of trimeric **9**; topview and sideview.

Table 1

Catalytic data for the Michael addition of  $\text{Et}_2\text{Zn}$  to 2-cyclohexenone in the absence and presence of 2 mol% of aminoarenethiolato copper(I) catalysts **1a**, **1b** and **9**<sup>a</sup>

Entry	Cu(I) complex	Solvent	Conversion <sup>b</sup> (%)
1	None	$\text{Et}_2\text{O}$	3
2	<b>1a</b>	$\text{Et}_2\text{O}$	>99
3	<b>1a</b>	Toluene	95
4	<b>1a</b>	THF	24
5	<b>1b</b>	$\text{Et}_2\text{O}$	>99
6	<b>9</b>	$\text{Et}_2\text{O}$	>99
7	<b>9</b>	Toluene	>99
8	<b>9</b>	THF	62
9	<b>9</b>	Hexane	>99
10	<b>9</b>	$\text{CH}_2\text{Cl}_2$	>99

<sup>a</sup> Reaction carried out in solvent (2 mL) at  $-20^\circ\text{C}$  in the presence of 1.2 eq.  $\text{Et}_2\text{Zn}$ , 2 mol% of catalyst.

<sup>b</sup> Determined by GC after 4 h.

decomposition of the catalyst, whereas a solution of **9** is still active after exposure to air.

The improved catalytic performance of the dendritic catalyst **9** as compared to **1a** can be ascribed to the presence of the dendritic wedge in this novel Cu(I) spe-

cies. First of all, the wedge has a stabilizing effect on the resting state of the catalyst. Second, the presence of a bulky carbosilane substituent could activate aggregate dissociation to provide catalyst–substrate as well as catalyst–substrate–reagent intermediates [29] from which product formation occurs. Finally, site isolation effects caused by the inert carbosilane wedge may be in operation, making deactivation of the catalyst by aggregation less likely.

#### 4. Conclusions

An aminoarenethiolato copper(I) compound was attached to a  $G_0$ -carbosilane dendritic wedge, which had been prepared via a novel convergent synthetic method. The convergent synthesis of the supported catalyst allows easy access to higher generations. By reduction of chlorosilane **5** with  $\text{LiAlH}_4$ , silane **10** was prepared. This silane can be used to react with trivinylchlorosilane **3** to obtain higher generation chlorosilane wedges, see Scheme 1. The introduction of the actual catalytic copper center can thus be postponed to the final step. Compared with the unsupported complex, the novel dendritic catalyst **9** is more robust towards water, has increased solubility in common organic solvents and its catalytic activity is comparable to that of the parent aminoarenethiolato copper(I) compound.

The improved solubility of the dendritic Cu(I) complex, even in apolar solvents such as hexane, allows the use of a wide variety of substrates that are not soluble in conventional solvents.

The increased stability and size of **9** allows separation of this catalyst by means of a nanofiltration membrane. Optimization of catalyst recycling requires synthesis of copper(I) catalysts with higher generation dendritic wedges. Research towards this goal is currently underway.

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