

# Isolable and Well-Defined Butadienyl Organocopper(I) Aggregates: Facile Synthesis, Structural Characterization, and Reaction Chemistry

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**S** Supporting Information

**ABSTRACT:** Four types of alkenyl organocopper(I) aggregates linked by 1,3-butadienyl and/or 1,3,5,7-octatetraenyl moieties were selectively realized in good isolated yields. All these organocopper(I) aggregates were structurally characterized by single-crystal X-ray structural analysis. These unprecedented aggregates, stabilized by multiple Cu–Cu interactions and the conjugated 1,3-butadienyl or 1,3,5,7-octatetraenyl bridges, could undergo controlled structural transformations. The 1,4-dicopper 1,3-butadienyl aggregate 3 could be efficiently transformed to aggregate 2, while LiI could disaggregate the 1,3-butadienyl-1,3,5,7-octatetraenyl aggregate 4 to 1,3,5,7-octatetraenyl aggregate 5 and 1,3-butadienyl aggregate 2. Preliminary reaction chemistry and synthetic applications of these organocopper(I) aggregates were also investigated.

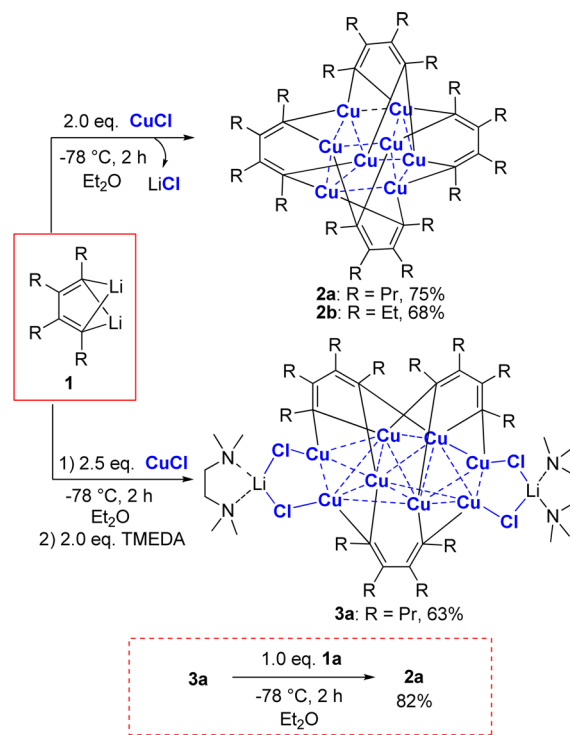
Organocopper compounds,<sup>1–5</sup> including diorganocuprates LiCuR<sub>2</sub>,<sup>2</sup> hetero-organocuprates MCuRX (M = Li, Cu, Ag; X = monoanionic group),<sup>3</sup> and organocopper(I) oligomers (CuR)<sub>n</sub>,<sup>4</sup> are structurally interesting and synthetically useful.<sup>1–5</sup> Among them, organocuprates have been well investigated and synthetically widely applied.<sup>1–3</sup> However, the study and characterization of organocopper compounds (CuR)<sub>n</sub> remains a great challenge, due to their thermal instability and low solubility in common organic solvents.<sup>4</sup> Although remarkable achievements have been realized in isolation and structural characterization of aryl,<sup>4</sup> alkynyl,<sup>5i</sup> and alkylorganocopper(I)<sup>4i</sup> compounds (CuR)<sub>n</sub> isolable and structurally well-defined alkenyl organocopper(I) compounds are basically unknown.<sup>6</sup> Since alkenylcopper compounds are often proposed as key intermediates in Cu-mediated or -catalyzed synthetic chemistry,<sup>7</sup> their isolation and structural elucidation are fundamentally important and synthetically attractive.

We have been studying reactivity, structural features, and synthetic application of 1,4-dilithio-1,3-butadienes (dilithio reagents).<sup>8,9</sup> Our results have demonstrated that the butadienyl skeleton shows remarkable cooperative stabilizing ability for reactive organometallic intermediates.<sup>8</sup> Hence, we envisioned that the butadienyl bridge would construct a favorable structure for achieving Cu–Cu interactions to stabilize the alkenyl-dicopper compounds. Herein we report the isolation and structural characterization of four different types of unprecedented alkenylcopper(I) compounds from the reaction

between dilithio reagents **1** and CuCl. Controlled structural transformations among these organocopper(I) aggregates were observed. Preliminary reaction chemistry and synthetic applications of these aggregates were investigated.

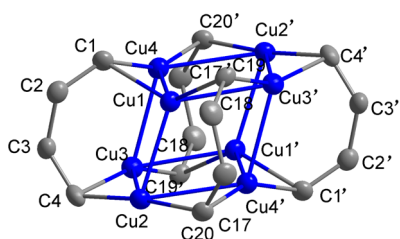
1,2,3,4-Tetrasubstituted 1,4-dilithio-1,3-butadienes **1** could be readily synthesized and isolated in high yields from the reaction between their corresponding diiodides and *t*-BuLi.<sup>9a,10</sup> Treatment of the tetrapropyl-substituted dilithio reagent **1a** (R = Pr) with 2.0 equiv of CuCl in Et<sub>2</sub>O at –78 °C for 2 h afforded the 1,4-dicopper-1,3-butadiene tetrameric compound **2a** in 75% isolated yield (Scheme 1). This compound **2a** was obtained as air- and moisture-sensitive red crystals and characterized by X-ray single-crystal structural analysis (Figure 1). For this tetrameric organo-dicopper aggregate, the eight

**Scheme 1. Synthesis of 1,3-Butadienyl Dicopper(I) Aggregates 2 and 3, and Their Structural Transformation**



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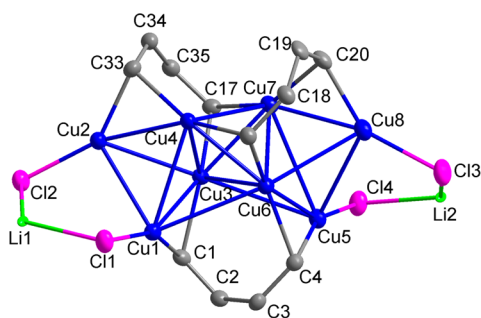
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**Figure 1.** Diamond drawing of **2a** with 30% thermal ellipsoids. Propyl substituents are omitted for clarity.

copper atoms form a slightly distorted hexahedral, and the four butadienyl moieties are linked to the copper cluster via two three-center-two-electron (3c-2e) bonds. The bridged 1,3-butadienyl ligands linked to four Cu atoms formed an approximate parallelogram with Cu1–Cu4 2.4708(10), Cu3–Cu4 2.4863(10), Cu1–Cu2 2.4966(11), and Cu2–Cu3 2.6694(10) Å. The Cu–Cu distances indicated  $d^{10}$  metal–metal interactions (2.45–3.10 Å).<sup>11</sup> The Cu–Cu stacking interaction stabilized the organo-dicopper compounds. Terminal carbons are each linked to two copper atoms in a 3c-2e bonding mode with  $C_{\text{ipso}}\text{--Cu}$  distances of 1.955(5), 2.081(5) and 1.961(5), 2.047(5) Å, respectively. The angles of Cu–C–Cu are 74.5–83.5°, and those C–Cu–C angles are 153.5–173.3°, indicating a nearly linear geometry. When the tetraethyl substituted dilithio reagent **1b** (R = Et) was used, compound **2b** was obtained in 68% isolated yield as light-red crystals. Although **2b** is also a tetramer, the configuration of copper clusters tended to be more distorted hexahedrally than **2a** (see Supporting Information [SI] for detail). However, the bond lengths and angles of **2b** are almost the same as those of **2a**. These results indicate that the substituents can influence the Cu–Cu stacking geometry but do not remarkably change the C–Cu bond distances.<sup>4h,i,k</sup>

A different type of organocopper(I) aggregate **3** was obtained when the dilithio reagent **1** was treated with an excess amount of CuCl (Scheme 1). When 2.5 equiv of CuCl was added into the Et<sub>2</sub>O solvent of **1a** at –78 °C, precipitation was obtained. The solid was filtered and recrystallized in Et<sub>2</sub>O with 2.0 equiv of TMEDA to give yellow crystals **3a** in 63% isolated yield. Single-crystal X-ray structural analysis shows that **3a** comprises eight copper atoms in a hexagonal close-packed arrangement which forms five tetrahedrons (Figure 2). There are two types of copper atoms; half of the copper atoms formed Cl–Cu–C bonds (Cu1, Cu2, Cu5, Cu8), and the others formed C–Cu–C bonds. Three 1,3-butadienyl ligands have different environments; the C1–C4 butadienyl ligand is a symmetrical one with



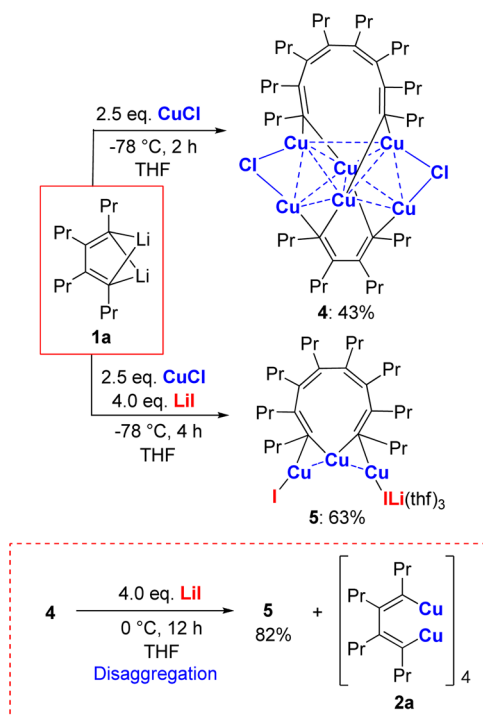
**Figure 2.** Diamond drawing of **3a** with 30% thermal ellipsoids. Propyl substituents and TMEDA are omitted for clarity.

each terminal carbon atom linked to the same type of Cu atom, while the C17–C20, C33–C36 butadienyl ligands are unsymmetrical, with two terminal carbons linked to different types of Cu atoms. These differences were also observed by their NMR spectra (see SI for detail). The distances of C–Cu bonds range from 1.959(6) Å to 2.016(5) Å which are similar to the reported values (1.95–2.15 Å),<sup>4,11</sup> while the Cu–Cl bonds range from 2.1545(15) Å to 2.1750(17) Å. The angles of 3c-2e Cu–C–Cu bonds range from 74.4° to 78.6°, which are similar to those for compounds **2a** and **2b**. The C–Cu bond distances and Cu–C–Cu angles for compound **3a** tend to be homogeneous because of the loose arrangement of the substituents.

The aggregate **3a** could be transformed to **2a** in 82% yield when treated with 1.0 equiv of **1a** in Et<sub>2</sub>O (Scheme 1).

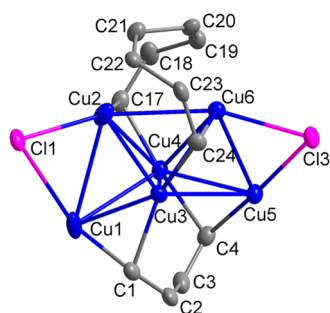
Interestingly, solvents and additives were found to influence the formation and structure of alkenyl dicopper(I) aggregates remarkably. As given in Scheme 2, when the dilithio reagent **1a**

### Scheme 2. Synthesis of 1,3,5,7-Octatetraenyl Dicopper(I) Aggregates **4** and **5**, and Their Structural Transformation/Disaggregation

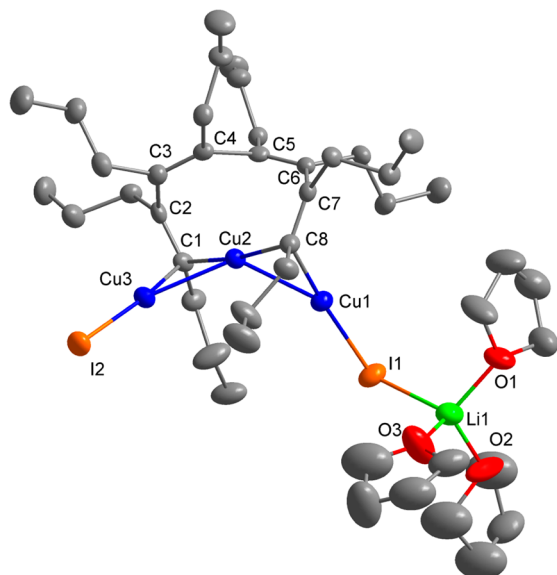


was treated with 2.5 equiv of CuCl in THF in place of Et<sub>2</sub>O, the aggregate **4** linked by 1,3-butadienyl and 1,3,5,7-octatetraenyl moieties was obtained in 43% isolated yield. Apparently, dimerization of 1,3-butadienyl 1,4-dicopper(I) moieties took place. When **1a** was treated with 2.5 equiv of CuCl and 4.0 equiv of LiI in THF, 1,8-dicopper-1,3,5,7-octatetraene derivative **5** was obtained in 63% isolated yield.<sup>12</sup> The LiI salt could disaggregate the dicopper complexes and increase their reactivity to give the dimerization product. When **4** was treated with 4.0 equiv of LiI in THF, disaggregation took place, affording **5** in 82% yield and a small amount of **2a** (Scheme 2).

The structures of **4** and **5** were both characterized by X-ray single-crystal structural analysis (Figures 3 and 4). Figure 3 shows that compound **4** contains six copper atoms, which form three tetrahedrons. There are two types of copper atoms, Cu3



**Figure 3.** Diamond drawing of **4** with 30% thermal ellipsoids. Propyl substituents are omitted for clarity.



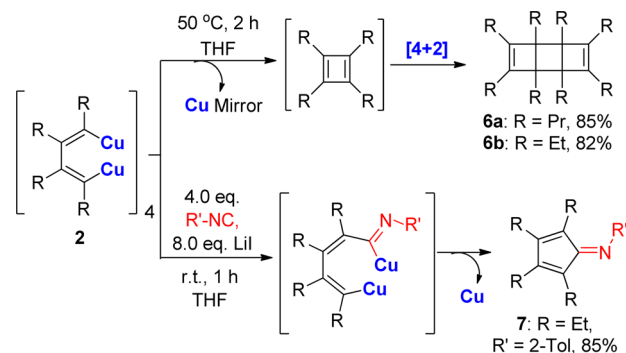
**Figure 4.** Diamond drawing of **5** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

and Cu4 atoms forming C–Cu–C bonds and the others forming C–Cu–Cl bonds. The terminal carbon atoms of 1,3,5,7-octatetraenyl and 1,3-butadienyl ligands are linked to the same type of copper atoms, respectively.

As shown in Figure 4, the compound **5** contains three copper atoms, which form a linear Cu–Cu–Cu coordination geometry. Each terminal carbon atom is linked with two copper atoms, forming three-center-two-electron (3c-2e) bonds with  $C_{\text{ipso}}-\text{Cu}$  distances in the range 1.974(5)–2.005(5) Å. The angles of Cu–C–Cu are 72.79(15)° and 75.23(17)°, respectively, which are similar to those for **2a**, **2b**, and **3a**. The favorable distance of octatetraenyl linker made **5** form a nine-membered copper-heterocycle and could also achieve the linear geometry of the C–Cu–C bond (C–Cu–C angle is 171.71(18)°). The distances of Cu–Cu bonds (2.3749(8) Å, 2.4192(8) Å) show stronger Cu–Cu interaction.<sup>11c</sup>

The reactivities of 1,4-dicopper **2** and 1,8-dicopper **5** aggregates were investigated. All the aggregated organocopper compounds **2**–**5** were thermally stable at solid states at room temperature under dry N<sub>2</sub>. Intramolecular homocoupling of **2** and subsequent [4 + 2] cycloaddition took place (Scheme 3), giving tricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-dienes **6** in high isolated yields.<sup>12,13</sup> Because LiI salt could disaggregate the copper complexes and increase their reactivity, in the presence of LiI, **2b** thus could react with 2-methylphenyl isocyanide to give the

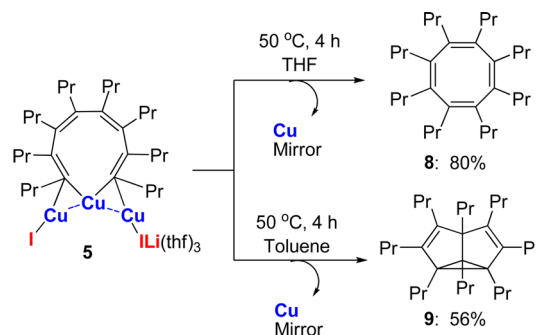
### Scheme 3. Demonstration of Reaction Chemistry of 1,4-Dicopper-1,3-butadiene Tetrameric Aggregates **2**



iminocyclopentadiene derivative **7** in 85% isolated yield via 1,1-insertion reaction followed by intramolecular coupling.

When the aggregate **5** was dissolved in THF, and the solution was heated to 50 °C (Scheme 4), an intramolecular

### Scheme 4. Thermal Transformation of 1,8-Dicopper-1,3,5,7-octatetraene Aggregate **5**



C–C coupling reaction proceeded, affording its corresponding cyclooctatetraene derivative **8** in 80% isolated yield with copper mirror.<sup>7k,14</sup> However, when the solvent was changed to toluene, the semibullvalene derivative **9** was obtained in 56% isolated yield along with a small amount of cyclooctatetraene **8**.<sup>7k</sup> The intermediacy of compound **5** was proposed for CuCl-mediated reactions of dilithio reagents in our early work.<sup>7k,13,14</sup>

In summary, we have synthesized and structurally characterized the first series of alkenylcopper(I) aggregates which contain two 3c-2e Cu–C–Cu bonds. The favorable distance of 1,3-butadienyl bridges is considered essential for achieving Cu–Cu interactions to stabilize the alkenylcopper compounds. Preliminary reaction chemistry and synthetic applications of these organocopper(I) aggregates were investigated.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, X-ray data for **2a**, **2b**, **3a**, **4**, **5** and scanned NMR spectra of all new products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.



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