

# Organocopper(III) Spiro Complexes: Synthesis, Structural Characterization, and Redox Transformation

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**S** Supporting Information

**ABSTRACT:** Reductive elimination of Cu(III) intermediates is often proposed as a key step in many copper-catalyzed or -mediated formation of C–C or C–heteroatom bonds. However, there still lacks concrete evidence on this key step, mainly because Cu(III) complexes are usually too unstable to be isolated and structurally characterized. In this work, novel organocopper(III) spiro complexes and their analogous organocopper(I) spiro complexes were synthesized and structurally characterized. Single-crystal X-ray structural analysis revealed that the spiro Cu(III) atom adopted a distorted square-planar geometry while its corresponding spiro Cu(I) atom was tetrahedrally coordinated. A redox transformation between these spiro Cu(I) and Cu(III) complexes was experimentally observed by reacting with reductants or oxidants, respectively. As concrete evidence, the organocopper(III) spiro compounds were found to form C–C bonds intramolecularly via reductive elimination.

Organocopper(III) compounds have been often proposed as key intermediates in many copper-catalyzed or -mediated synthetic organic reactions.<sup>1</sup> In these reactions, reductive elimination of organocopper(III) compounds is considered as the final step leading to the formation of C–C or C–heteroatom bonds. However, well-defined structures of organocopper(III) compounds remain rather limited to date, which results in the lack of concrete evidence on the reductive elimination of Cu(III) complexes. Although a few of tetra-carbon-coordinated organocuprates(III) have been reported,<sup>2–4</sup> the majority of successful examples are porphyrin-supported Cu(III) complexes or macrocyclic chelating ligand-stabilized Cu(III) complexes,<sup>5,6</sup> since Cu(III) atom prefers square-planar coordination. Unfortunately, all the above-mentioned works did not give concrete experimental evidence for the reductive elimination of Cu(III) species to form C–C bonds.<sup>7</sup>

In recent years, we have been studying on the chemistry of 1,3-butadiene-based organocopper compounds. Treatment of tetra-alkyl-substituted 1,4-dilithio-1,3-butadienes (dilithio reagent for short) with excess CuCl in Et<sub>2</sub>O or THF solvent afforded a variety of organocopper(I) aggregates.<sup>8</sup> On the other hand, the reaction between bulky  $\alpha$ -trimethylsilyl substituted dilithio reagents and CuCl in mixed Et<sub>2</sub>O/hexane solvent

afforded aromatic dicupra[10]annulenes.<sup>9</sup> As our continued interest in organocopper chemistry, herein we report the synthesis, structural characterization and reaction chemistry of aryl Cu(I) and Cu(III) spiro ate complexes.<sup>10</sup> A redox transformation between these spiro Cu(I) and Cu(III) complexes was experimentally observed. Most importantly, the organocopper(III) spiro compounds were found to form C(sp<sup>2</sup>)–C(sp<sup>2</sup>) bonds intramolecularly, along with generation of their corresponding Cu(I) species, which presents concrete evidence on the reductive elimination of Cu(III) complexes.

Dilithio reagents **1** were readily prepared in a modified procedure of the literature.<sup>11</sup> As shown in eq 1 of Scheme 1, the reaction of biphenyl dilithio reagent **1a** with 0.5 equiv of CuBr·SMe<sub>2</sub> in THF at room temperature for 1.5 h afforded a black solution. The spiro organocuprate(I) **2a** was produced in almost quantitative yield, as determined by <sup>1</sup>H NMR spectroscopy in THF-*d*<sub>8</sub>. After recrystallization in THF at room temperature, **2a** was obtained as dark-red crystals in 75% isolated yield.

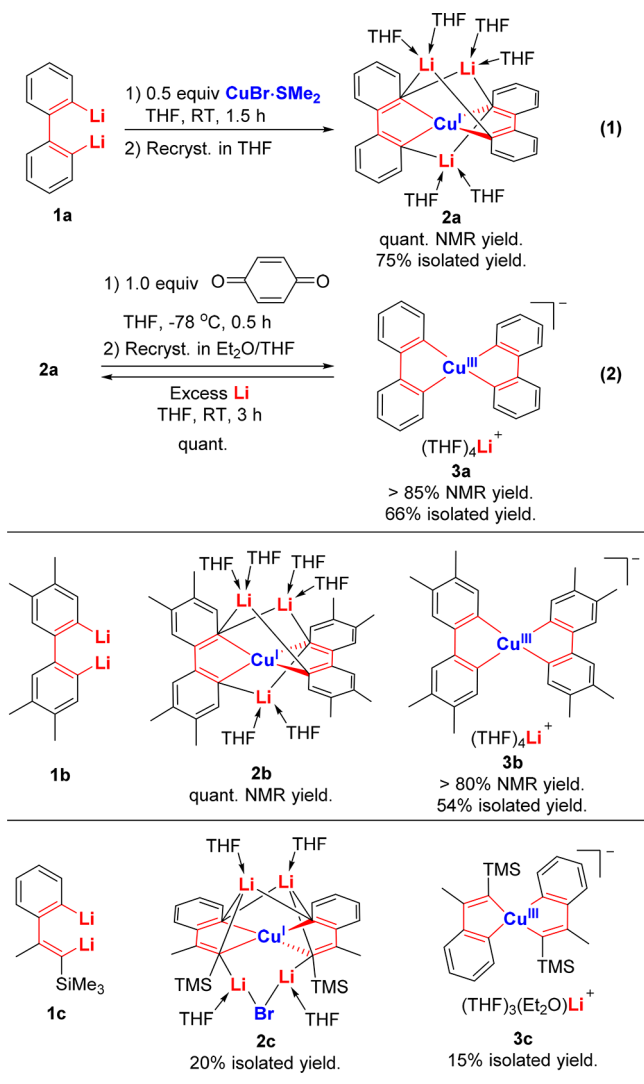
As shown in eq 2 of Scheme 1, treatment of **2a** with a stoichiometric amount of oxidants, such as *p*-benzoquinone, iodides, 1-fluoropyridinium tetrafluoroborate or molecular oxygen, all produced the spiro organocuprate(III) **3a** in more than 85% yield, as determined by <sup>1</sup>H NMR spectroscopy. After recrystallization in THF at –10 °C, **3a** was obtained as light-yellow crystals in 66% isolated yield. In return, **3a** could be reduced with an excess amount of metal lithium to regenerate **2a** quantitatively, as determined by <sup>1</sup>H NMR spectroscopy.

Similarly, the dilithio reagent **1b** could be also applied, affording its corresponding spiro organocuprate(I) **2b** (Scheme 1). The above redox transformation also took place, which afforded its corresponding spiro organocuprate(III) **3b** in 54% isolated yield. **3b** could be also quantitatively reduced to regenerate **2b**. In the case of vinylphenyl dilithio reagent **1c** (Scheme 1), the corresponding **2c** and **3c** could be also obtained, but with much lower yields, probably due to their decomposition to benzosilyl species or homocoupling compounds of vinylphenyl fragments.<sup>12</sup> It should be noted that, in addition to CuBr·SMe<sub>2</sub>, CuCl, and CuI could also be applied to the above reactions, affording spiro Cu(I) ate complexes in comparable yields.

Received: August 18, 2017

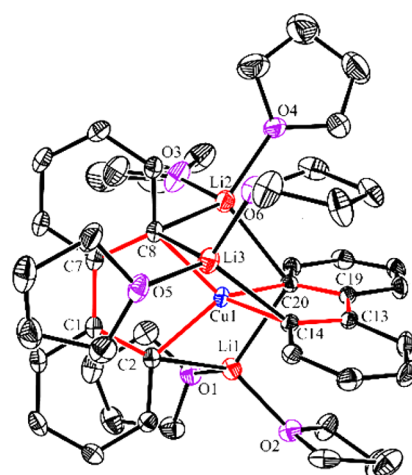
Published: September 21, 2017

## Scheme 1. Synthesis of Organocopper(I) Spiro Compounds 2 and Organocopper(III) Spiro Compounds 3

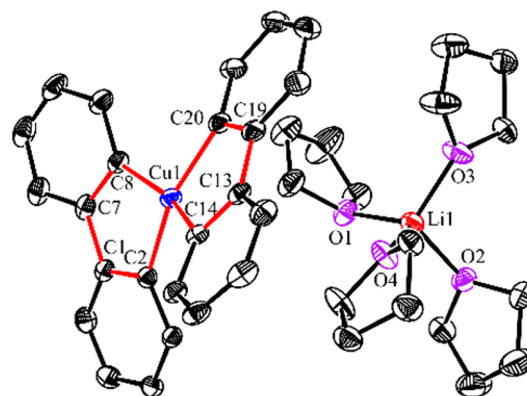


The molecular structures of **2a**, **2c**, and **3a–c** were all confirmed by X-ray crystallographic analysis (see [Supporting Information](#) for details). Crystallized in the triclinic  $P1$  space group, **2a** consists of one Cu(I) atom, two biphenyl ligands and three  $\text{Li}(\text{THF})_2$  moieties ([Figure 1](#)). The Cu(I) atom is tetra-coordinated with four carbon atoms of biphenyl ligands. The Cu(I) center adopted a slightly distorted tetrahedral geometry with a dihedral angle of  $84.1(1)^\circ$  between spiro-fused two 5-membered cupracycles. The lengths of Cu(I)–C( $\text{sp}^2$ ) bonds [ $2.030(3)$ – $2.040(3)$  Å] range in the value of previously reported organocuprates in the literature,<sup>13</sup> while the bite angles of C–Cu(I)–C (*cis*-bonds) in the 5-membered rings are  $86.6(1)^\circ$  and  $86.8(1)^\circ$ , respectively. The lithium atoms are all tetra-coordinated with two THF and two carbon atoms of separated biphenyl ligands. Spiro Cu(I) complex **2a** is a rare example of high-order organocuprates(I),<sup>13</sup> simply described as  $\text{R}_n\text{CuLi}_{n-1}$  ( $n > 2$ ), in which the Cu(I) atom is linked with more than two organo groups.

The compound **3a** was crystallized in the monoclinic  $P2_1/c$  space group. As [Figure 2](#) displays, **3a** is a solvent-separated ion pair, which comprises one Cu(III) atom, two biphenyl ligands, and one lithium counteranion moiety. The Cu(III) atom is linked with four carbon atoms with a  $27.2(5)^\circ$  dihedral



**Figure 1.** ORTEP drawing of **2a** with thermal ellipsoids plots drawn at 30% probability. All H atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]: C2–Cu1 2.035(3), C8–Cu1 2.040(3), C14–Cu1 2.035(3), C20–Cu1 2.030(3); C2–Cu1–C8 86.6(1), C14–Cu1–C20 86.8(1), C2–Cu1–C14 115.5(1), C2–Cu1–C20 125.1(1), C8–Cu1–C14 125.1(1), C8–Cu1–C20 122.0(1).



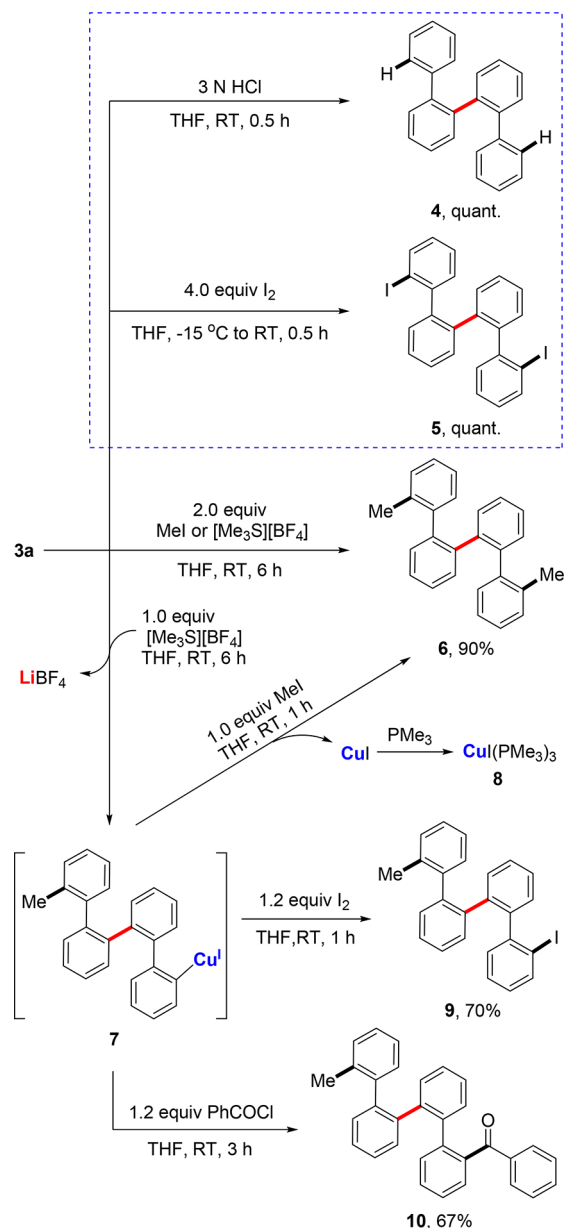
**Figure 2.** ORTEP drawing of **3a** with thermal ellipsoids plots drawn at 30% probability. All H atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]: C2–Cu1 1.954(3), C8–Cu1 1.968(3), C14–Cu1 1.952(3), C20–Cu1 1.965(3); C2–Cu1–C8 83.9(1), C14–Cu1–C20 83.9(1), C2–Cu1–C14 96.2(1), C2–Cu1–C20 163.3(1), C8–Cu1–C14 160.2(1), C8–Cu1–C20 101.6(1).

angle between two 5-membered rings, indicating a nearly square-planar coordination for the central Cu(III) atom. The lengths of Cu(III)–C( $\text{sp}^2$ ) bonds [ $1.952(3)$ – $1.968(3)$  Å] are parallel to those of previously reported Cu(III) compounds<sup>2,4–6</sup> and slightly shorter than those of Cu(I)–C( $\text{sp}^2$ ) bonds of **2a**, in accordance with the trend that the valence increases, the radius of copper atoms gets smaller. The *cis*-bonding angle [ $83.9(1)^\circ$ ] of C–Cu(III)–C of **3a** is so far the sharpest C–Cu(III)–C angles among all reported data in the literature. Since the *meta*- and *para*-methyl substituents of biphenyl ligands in **3b** posed no steric effects in the structure, the dihedral angle [ $29.2(1)^\circ$ ] of **3b** was almost identical to that of **3a**. **3c** adopted a more distorted square-planar geometry with the dihedral angle of [ $37.9(4)^\circ$ ], probably due to the steric hindrance of 2-trimethylsilyl groups. These spiro compounds **3** are unprecedented and represent a novel type of organocopper(III) complexes.

With the spiro organocuprate(III) complexes in hand, we then had very much interest in their reaction chemistry,

especially their reductive elimination reaction, because it could shed light on the mechanism of Cu-catalyzed or -mediated C–C bond-forming reactions, in which organocopper(III) compounds have been often proposed as key intermediates (Scheme 2). Surprisingly, **3a** was thermally very stable under

Scheme 2. Reductive Elimination of **3a**



nitrogen atmosphere. It could remain intact even after reflux in THF for 12 h. Finally, we found that **3a** did undergo the potential reductive elimination reactions when treated with electrophiles. Thus, as shown in Scheme 2, the *o*-quaterphenyl **4** was obtained in a quantitative isolated yield when **3a** was quenched with 3 N HCl at room temperature.<sup>14</sup> Treatment of **3a** with excess I<sub>2</sub> quantitatively produced the diiodo-*o*-quaterphenyl **5**,<sup>10a</sup> which is expected to be useful for further functionalization (for the crystal structure of **5**, see Figure S6 of the Supporting Information).

In order to further investigate the reaction mechanisms of the intramolecular C(sp<sup>2</sup>)–C(sp<sup>2</sup>) bond-forming reactions, the

reaction between **3a** and methylation reagents was then conducted (Scheme 2). **3a** reacted with 2.0 equiv of methyl iodide or trimethylsulfonium fluoroborate to produce dimethyl-*o*-quaterphenyl **6** in 90% isolated yield.<sup>14</sup> Treatment of **3a** with 1.0 equiv of trimethylsulfonium fluoroborate mainly afforded the intermediate **7**, an arylcopper(I) species, along with a tiny amount of **6**. Although the attempt to isolate and characterize the intermediate **7** was failed, the *in situ* generated solution of **7** was found to react with 1.0 equiv of methyl iodide to produce **6** also in about 90% overall yield. When PMe<sub>3</sub> was added to this solution before workup, CuI(PMe<sub>3</sub>)<sub>3</sub> (**8**) was isolated from THF solution and determined by single-crystal analysis (for the crystal structure of **8**, see Figure S7 of the Supporting Information). Additionally, the *in situ* generated solution of **7** reacted with 1.2 equiv of I<sub>2</sub> or benzoyl chloride to afford the monomethyl-monoiodo-*o*-quaterphenyl **9** and the monomethyl-mono-phenylacyl-*o*-quaterphenyl **10** in 70% and 67% isolated yields, respectively. The high-yield formation of **6**, **8**, **9**, and **10** strongly supported the existence of the intermediate **7**. These experimental results presented direct evidence for the reductive elimination of spiro Cu(III) complex **3a**. Consequently, the C(sp<sup>2</sup>)–C(sp<sup>2</sup>) bond-forming process might proceed via an electrophilic attack from methylation reagents to **3a** and a further reductive elimination reaction of Cu(III) intermediate.

In summary, we have synthesized, isolated, and structurally characterized a series of unprecedented spiro organocuprates(I) and spiro organocuprates(III) complexes. The reaction chemistry study of spiro organocopper(III) compounds provides concrete evidence on the reductive elimination of Cu(III) complexes. This work is fundamentally significant for understanding the mechanism of Cu(III)-involved synthetic organic reactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08803.

Experimental details and NMR spectra of new products (PDF)

X-ray data for **2a**, **2c**, **3a–3c**, **5**, and **8** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21372012, 21690061).

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