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Communication

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

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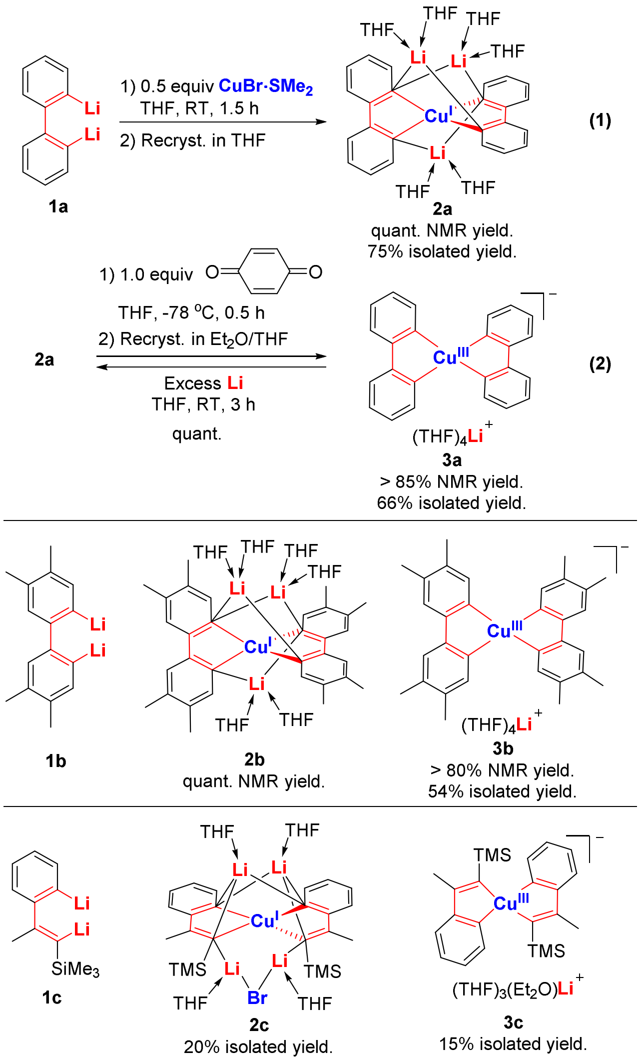
Supporting Information Placeholder

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-catalysed or -mediated synthetic organic reactions.[1] 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,[2-4] the majority of successful examples are porphyrin-supported Cu(III) complexes or macrocylic cheleting ligand-stabilized Cu(III) complexes,[5,6] 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.[7]

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_2O or THF solvent afforded a variety of organocopper(I) aggregates.[8] On the other hand, the reaction between bulky *α*-trimethylsilyl substituted dilithio reagents and CuCl in mixed Et_2O/Hexane solvent afforded aromatic dicupra[10]annulenes.[9] 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.[10] A redox transformation between these spiro Cu(I) and Cu(III) complexes was experimentally observed. Most

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



importantly, the organocopper(III) spiro compounds were found to form C(sp^2)–C(sp^2) 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.[11] As shown in eq. (1) of Scheme 1, the reaction of biphenyl dilithio reagent **1a** with 0.5 equiv of CuBr•SMe_2 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 ^{1}H NMR spectroscopy in d^8-THF. 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 ^{1}H NMR spectroscopy. After recrystallization in THF at -10 ºC, **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 ^{1}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 benzosilolyl species or homo-coupling compounds of vinylphenyl fragments.[12] It should be noted that, in addition to CuBr•SMe_2, CuCl and CuI could also be applied to the above reactions, affording spiro Cu(I) ate complexes in comparable yields.

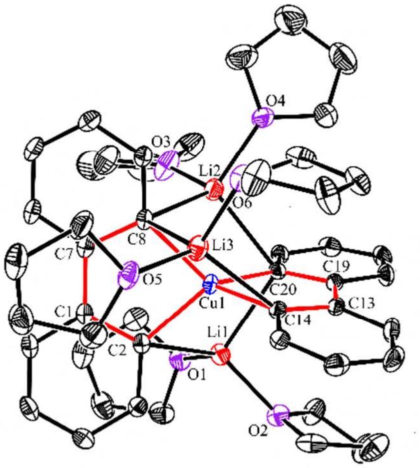


Figure 1. ORTEP drawing of **2a** with thermal ellipsoids plots drawn at 30% probability. All H atoms were omitted for clarity. Selected bond lengths [Å] and angles [º]: C2–Cu1 2.035(3), C8–Cu1 2.040(3), C14–Cu1 2.035(3), C20–Cu1 2.030(3); C2-Cu1-C8 86.6(1), C14-Cu1-C20 86.8(1), C2-Cu1-C14 115.5(1),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

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 P-1 space group, **2a** consists of one Cu(I) atom, two biphenyl ligands and three $Li(THF)_2$ 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)º between spiro-fused two 5-membered cupracycles. The lengths of Cu(I)–C(sp^2) bonds [2.030(3)-2.040(3) Å] range in the value of previously reported organocuprates in the literature,[13] while the bite angles of C-Cu(I)-C (*cis*-bonds) in the 5-membered rings are 86.6(1)º and 86.8(1)º, 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),[13] simply described as R_nCuLi_{n-1} ($n > 2$), in which the Cu(I) atom is linked with more than two organo groups.

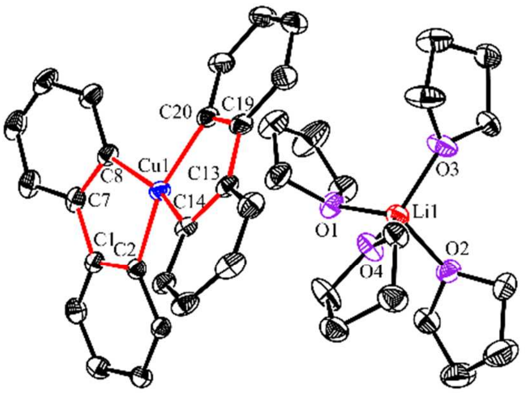


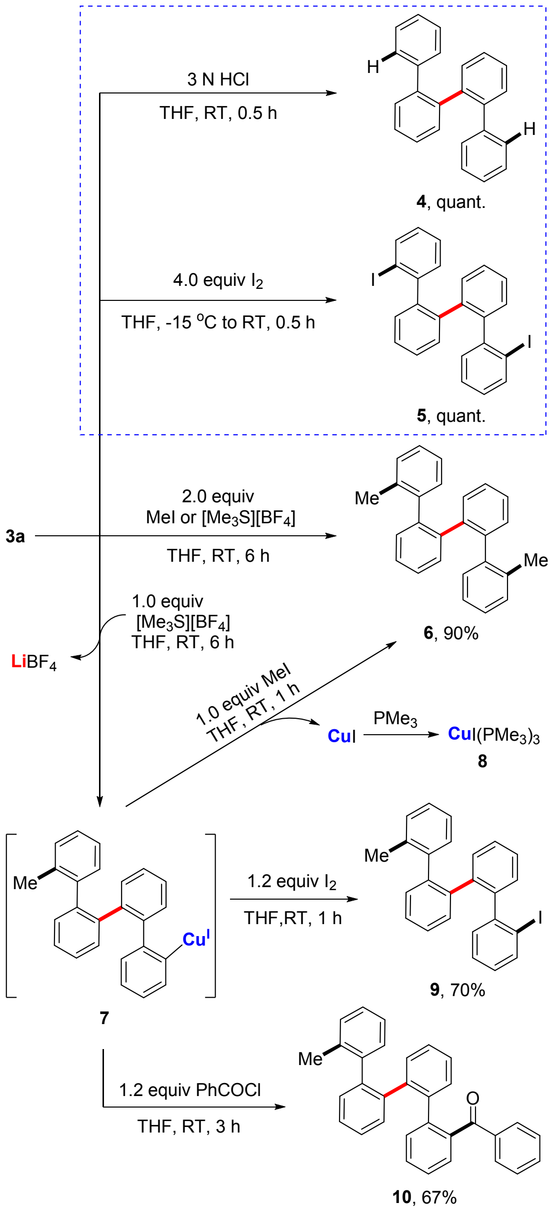
Figure 2. ORTEP drawing of **3a** with thermal ellipsoids plots drawn at 30% probability. All H atoms were omitted for clarity. Selected bond lengths [Å] and angles [º]: C2–Cu1 1.954(3), C8–Cu1 1.968(3), C14–Cu1 1.952(3), C20–Cu1 1.965(3); C2-Cu1-C8 83.9(1), C14-Cu1-C20 83.9(1), C2-Cu1-C14 96.2(1), C2-Cu1-C20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

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 compromises one Cu(III) atom, two biphenyl ligands and one lithium counter-cation moiety. The Cu(III) atom is linked with four carbon atoms with a 27.2(5)º dihedral angle between two 5-membered rings, indicating a nearly square-planar coordination for the central Cu(III) atom. The lengths of Cu(III)–C(sp^2) bonds [1.952(3)-1.968(3) Å] are parallel to those of previously reported Cu(III) compounds[2,4-6] and slightly shorter than those of Cu(I)–C(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)º] 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)º] 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)º], 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 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.[14] Treatment of **3a** with excess I_2 quantitatively produced the diiodo-*o*-quaterphenyl **5**,[10a] which is expected to be useful for further functionalization (for the crystal structure of **5**, see SFigure 6 of Supporting Information).

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



In order to further investigate the reaction mechanisms of the intramolecular C(sp^2)–C(sp^2) 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.[14] 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_3 was added to this solution before workup, $CuI(PMe_3)_3$ (**8**) was isolated from THF solution and determined by single-crystal analysis (for the crystal structure of **8**, see SFigure 7 of Supporting Information). Additionally, the *in situ* generated solution of **7** reacted with 1.2 equiv of I_2 or benzoyl chloride to afford the monomethyl-monoiodo-*o*-quaterphenyl **9** and the monomethyl-monophenylacyl-*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^2)–C(sp^2) 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

Experimental details, X-ray data for **2a**, **2c**, **3a-3c**, **5** and **8** and NMR spectra of 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 interests.

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REFERENCES

(1) (a) Sperotto, E.; van Klink, G. P. M.; van Koten, G.; de Vries, J. G. *Dalton Trans*. **2010**, *39*, 10338-10351. (b) Wendlandt, A. E.; Suess, A. M.; Stahl, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 11062-11087. (c) Hickman, A. J.; Sanford, M. S. *Nature* **2012**, 177-185. (d) Yoshikai, N.; Nakamura, E. *Chem. Rev*. **2012**, *112*, 2339-2372. (e) van Koten, G. *Organometallics* **2012**, *31*, 7634-7646. (f) Casitas, A.; Ribas, X. *Chem. Sci*. **2013**, *4*, 2301-2318. (g) Sambiagio, C.; Marsden, S. P.; Blacker, A. J.; McGowan, P. C. *Chem. Soc. Rev*. **2014**, *43*, 3525-3550. (h) McCann, S. D.; Stahl, S. *Acc. Chem. Res*. **2015**, *48*, 1756-1766.

(2) For perfluroalkyl Cu(III) complexes, see: (a) Willert, M. A.; Burton, D. J.; Baenziger, N. C. *J. Chem. Soc., Chem. Commun*. **1989**, 1633-1634. (b) Naumann, D.; Roy, T.; Tebbe, K.-F.; Crump, W. *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1482-1483. (c) Schlueter, J. A.; Geiser, U.; Williams, J. M.; Wang, H. H.; Kwok, W.-K.; Fendrich, J. A.; Carlson, K. D.; Achenbach, C. A.; Dudek, J. D.; Naumann, D.; Roy, T.; Schirber, J. E.; Bayless, W. R. *J. Chem. Soc., Chem. Commun*. **1994**, 1599-1600. (d) Eujen, R.; Hoge, B.; Brauer, D. J. *J. Organomet. Chem*. **1996**, *519*, 7-20. (e) Romine, A. M.; Nebra, N.; Konovalov, A. I.; Martin, E.; Benet-Buchholz, J.; Grushin, V. V. *Angew. Chem. Int. Ed*. **2015**, *54*, 2745-2749.

(3) For carborate-based Cu(III) complexes, see: (a) Wing, R. M. *J. Am. Chem. Soc*. **1968**, *90*, 4828-4834. (b) Varadarajan, A.; Johnson, S. E.; Gomez, F. A.; Chakrabarti, S.; Knobler, C. B.; Hawthorne, M. F.

J. Am. Chem. Soc. **1992**, *114*, 9003-9011. (c) Harwell, D. E.; McMillan, J.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem*. **1997**, *36*, 5951-5955.

(4) García-López, G.; Yañez-Rodíguez, V.; Roces, L.; Garcia-Granda, S.; Martinez, A.; Guevara-García, A.; Castro, G. R.; Jiménez-Villacorta, F.; Iglesias, M. J.; Ortiz, F. L. *J. Am. Chem. Soc*. **2010**, *132*, 10665-10667.

(5) For Cu(III) complexes supported by porphyrins or their analogs, see: (a) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc*. **2000**, *122*, 803-807. (b) Maeda, H.; Ishikawa, Y.; Matsuda, T.; Osuka, A.; Furuta, H. *J. Am. Chem. Soc*. **2003**, *125*, 11822-11823. (c) Maeda, H.; Osuka, A.; Furuta, H. *J. Am. Chem. Soc*. **2003**, *125*, 15690-15691. (d) Maeda, H.; Morimoto, T.; Osuka, A.; Furuta, H. *Chem. – Eur. J*. **2006**, *1*, 832-844. (e) Pawlicki, M.; Kańska, I.; Latos-Grażyński, L. *Inorg. Chem*. **2007**, *46*, 6575-7584. (f) Poater, A.; Cavallo. L. *Inorg. Chem*. **2009**, *48*, 2340-2342. (g) Adinarayana, B.; Thomas, A. P.; Suresh, C. H.; Srinivasan, A. *Angew. Chem. Int. Ed*. **2015**, *54*, 10478-10482.

(6) For Cu(III) complexes stablized by macrocylic cheleting ligands, see: (a) Ribas, X.; Jackson, D. A.; Donnadieu, B.; Mahía, J.; Parella, T.; Xifra, R.; Hedman, B.; Hodgson, K. O.; Llobet, A.. Stack, T. D. P. *Angew. Chem. Int. Ed*. **2002**, *41*, 2991-2994. (b) Xifra, R.; Ribas, X.; Llobet, A.; Poater, A.; Duran, M.; Sola, M.; Stack, T. D. R.; Benet-Buchholz, J.; Donnadieu, B.; Mahía, J.; Parella, T. *Chem. – Eur. J*. **2005**, *11*, 5146-5156. (c) Yao, B.; Wang, D.-X.; Huang, Z.-T.; Wang, M.-X. *Chem. Commun*. **2009**, 2899-2901. (d) King, A. E.; Huffman, L. M.; Casita, A.; Costas, M.; Ribas, X.; Stahl, S. S. *J. Am. Chem. Soc*. **2010**, *132*, 12068-12073. (e) Zhang, H.; Yao, B.; Zhao. L.; Wang, D.-X.; Xu, B.-Q.; Wang, M.-X. *J. Am. Chem. Soc*. **2014**, *136*, 6326-6332.

(7) For C–C bond or C–heteroatom bond formation from Cu(III) complexes based on macrocylic cheleting ligands when treated with nucleophiles, see: (a) Huffman, L. M.; Stahl, S. S. *J. Am. Chem. Soc*. **2008**, *130*, 9196-9197. (b) Casitas, A.; King, A. E.; Parella, T.; Costas, M.; Stahl, S. S.; Ribas, X. *Chem. Sci*. **2010**, *1*, 326-330. (c) Casitas, A.; Poater, A.; Solà, M.; Stahl, S. S.; Costas, M.; Ribas, X. *Dalton Trans*. **2010**, *39*, 10458-10463. (d) Huffman, L. M.; Casitas, A.; Font, M.; Canta, M.; Costas, M.; Ribas, X.; Stahl, S. S. *Chem. – Eur. J*. **2011**, *17*, 10643-10650. (e) Huffman, L. M.; Stahl, S. S. *Dalton Trans*. **2011**, *40*, 8959-8963. (f) Casitas, A.; Ioannidis, N.; Mitrikas, G.; Costas, M.; Ribas, X. *Dalton Trans*. **2011**, *40*, 8796-8799. (g) Casitas, A.; Canta, M.; Solà, M.; Costas, M.; Ribas, X. *J. Am. Chem. Soc*. **2011**, *133*, 19386-19392. (h) Wang, Z.-L.; Zhao, L.; Wang, M.-X. *Org. Lett*. **2011**, *13*, 6560-6563. (i) Yao, B.; Wang, Z.-L.; Zhang, H.; Wang, D.-X.; Zhao, L.; Wang, M.-X. *J. Org. Chem*. **2012**, *77*, 3336-3340. (j) Wang, Z.-L.; Zhao, L.; Wang, M.-X. *Chem. Commun*. **2012**, *48*, 9418-9420. (k) Wang, Z.-L.; Zhao, L.; Wang, M.-X. *Org. Lett*. **2012**, *14*, 1472-1475. (l) Font, M.; Parella, T.; Costas, M.; Ribas, X. *Organometallics* **2012**, *31*, 7976-7982. (m) Zhang, H.; Zhao, L.; Wang, D.-X.; Wang, M.-X. *Org. Lett*. **2013**, *15*, 3836-3839. (n) Rovira, M.; Font, M.; Acuña-Parés, F.; Parella, T.; Luis, J. M.; Lloret-Fillol, J.; Ribas, X. *Chem. – Eur. J*. **2014**, *20*, 10005-10010.

(8) Geng, W.; Wei, J.; Zhang, W.-X.; Xi, Z. *J. Am. Chem. Soc*. **2014**, *136*, 610-613.

(9) Wei, J.; Zhang, Y.; Chi, Y.; Liu, L.; Zhang, W.-X.; Xi, Z. *J. Am. Chem. Soc*. **2016**, *138*, 60-63.

(10) a) Formation of organocopper spiro compounds was proposed fifty years ago. See: Wittig, G.; Klar, G. *Justus Liebigs Ann. Chem*. **1967**, *704*, 91-108. For spiro transition metal organometallic complexes, see: b) Jonas, K.; Burkart, G.; Häselhoff, C.; Betz, P.; Krüger, C. *Angew. Chem. Int. Ed. Engl*. **1990**, *29*, 322-323. c) Fröhlich, H.-O.; Wyrwa, R. *J. Organomet. Chem*. **1992**, *441*, 169-175. d) Fröhlich, H.-O.; Kosan, B. *J. Organomet. Chem*. **1992**, *441*, 177-184. e) Fröhlich, H.-O.; Wyrwa, R. *J. Organomet. Chem*. **1993**, *456*, 7-12. f) Fröhlich, H.-O.; Wyrwa, R.; Görls, H. *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 387-388. g) Wyrwa, R.; Fröhlich, H.-O.; Görls, H. *J. Organomet. Chem*. **1995**, *491*, 41-46. h) Wyrwa, R.; Fröhlich, H.-O.; Görls, H. *Z. Anorg. Allg. Chem*. **2000**, *626*, 819-821. i) Carnes, M.; Buccella, D.; Chen, J. Y.-C.; Ramirez, A. P.; Turro, N. J.; Nuckolls, C.; Steigerwald, M. *Angew. Chem. Int. Ed*. **2009**, *48*, 290-294. j) Wei, J.; Zhang, Y.; Zhang, W.-X.; Xi, Z. *Angew. Chem. Int. Ed*. **2015**, *54*, 9986-9990. k) Zhang, Y.; Wei, J.; Chi, Y.; Zhang, X.; Zhang, W.-X.; Xi, Z. *J. Am. Chem. Soc*. **2017**, *139*, 5039-5042.

(11) (a) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun*. **1982**, 1184-1185. (b) Liu, L.; Zhang, W.-X.; Luo, Q.; Li, H.; Xi, Z. *Organometallics* **2010**, *29*, 278-281.

(12) Luo, Q.; Wang, C.; Gu, L.; Zhang, W.-X.; Xi, Z. *Chem. – Asian J*. **2010**, *5*, 1120-1128. *Note*: **2c** was converted to benzosilolyl species and methyl lithium in d^8-THF at RT for 12 h almost in quantitative yield, as determined by ^{1}H NMR spectroscopy.

(13) Davies, R. P. *Coord. Chem. Rev*. **2011**, *255*, 1226-1251.

(14) a) He, J.; Crase, J. L.; Wadumethrige, S. H.; Thakur, K.; Dai, L.; Zou, S.; Rathore, R.; Hartley, C. S. *J. Am. Chem. Soc*. **2010**, *132*, 13848-13857. b) Zhang, Y.; Han, J.; Liu, Z.-J. *J. Org. Chem*. **2016**, *81*, 1317-1323.

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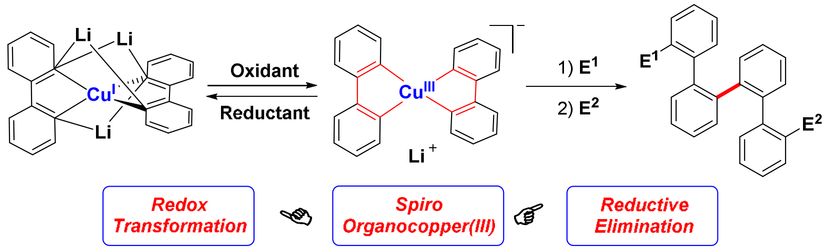
Li
Li
Cu^{I}
Li
Oxidant
Reductant
Cu^{III}
Li^{+}
1) E^{1}
2) E^{2}
E^{1}
E^{2}
Redox Transformation
Spiro Organocopper(III)
Reductive Elimination