Aromatic Dicupra[10]annulenes

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Ⓢ *Supporting Information*

ABSTRACT: Metal-containing aromatic systems (metalla-aromatics) are unique and important both experimentally and theoretically. Among metalla-aromatics, six-membered metallabenzenes and metallabenzynes have attracted much attention in recent years. However, reports on their superior homologues are rare. In this work, the first series of aromatic dicupra[10]annulenes were isolated from the reaction of dilithio reagents and copper salts. Single-crystal X-ray structural analysis revealed dicupra[10]annulenes with averaged bond lengths. ^{7}Li NMR spectra and theoretical calculations revealed considerable aromatic character. XPS data suggested that the oxidation state of Cu atom in dicupra[10]annulenes was more likely to be Cu(I), indicating that the dilithio moieties in dicupra[10]annulenes participated as noninnocent ligands. This work demonstrates a novel approach to construct macrocyclic metalla-aromatics.

The chemistry of metal-containing aromatics has long been a fundamental and fascinating topic. In recent years, a variety of metallabenzenes, metallabenzynes and their analogues have been elegantly synthesized and characterized.[1,2] However, although unique and useful chemical and physical properties can be expected, reports on their superior homologues are rare, probably due to lack of efficient synthetic methods. In fact, only three types of macrocyclic metalla-aromatics have been well-characterized: (1) metallanaphthalenes with osmium or iridium,[3] (2) osmanaphthalynes,[3b,4] (3) osmapentalenes and osmapenta-lynes.[2e,g,5] Therefore, the synthesis of macrocyclic metalla-aromatics with different metals still remains a great challenge.

Annulenes, which usually have a general formula $C_{2n}H_{2n}$, are classic cyclic conjugated systems and have been well studied.[6] The well-known annulenes include cyclobutadiene, benzene, and cyclooctatetraene (Figure 1). Based on the Hückel rule, they are
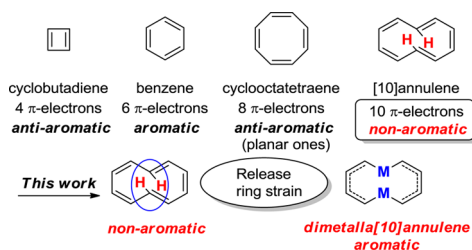

Figure 1. Concept of dimetalla[10]annulene.

antiaromatic, aromatic, and antiaromatic (planar ones),[6d] respectively. However, the [10]annulene having 10 π-electrons is nonaromatic, due to the steric hindrance of the two internal hydrogens. To release the steric hindrance of [10]annulene, we considered replacing the two internal C−H fragments with transition metals. If each of the two metals could offer one electron to form delocalized π-bonds, then the dimetalla[10]-annulene could be aromatic.

We have been working on the synthetic applications of multiply substituted 1,4-dilithio 1,3-butadienes (dilithio reagents for short) 1.[7] Recently, we found that appropriate dilithio reagents could react with low-valent transition metals, offering aromatic dilithio-metalloles,[8] in which the dilithio reagents behaved as noninnocent ligands. Inspired by the novel behavior of dilithio reagents, we envisioned that macrocyclic metalla-aromatics could be obtained by annulating two or more dilithio reagents with suitable transition metals. Herein we report the synthesis, characterization, and theoretic study of macrocyclic metalla-aromatics, dicupra[10]annulenes.

A successful trial is shown in Scheme 1. The reaction between dilithio reagents 1 and Cu(I) salts was carried out in the mixture

Scheme 1. Synthesis of Dicupra[10]annulenes 2 via Dilithio Reagents 1 and Copper Salts
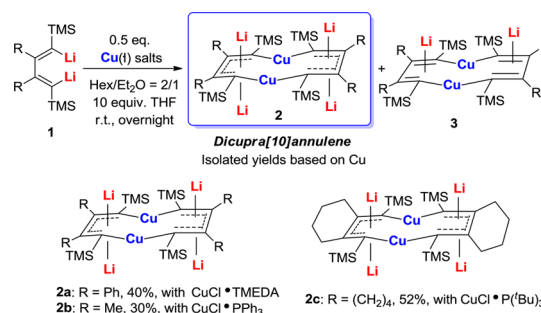
of hexane and diethyl ether at room temperature for 0.5 h, which was followed by addition of 10 equiv of tetrahydrofuran (THF). Dicupra[10]annulenes 2a−c were thus obtained in moderate isolated yields as dark red solids after recrystallizing in the mixture of THF and hexane. These compounds were air-sensitive, but thermally stable under inert conditions. Along with formation of the dicupra[10]annulenes 2, the compounds 3 were also observed as byproducts in small amounts (about 5−10%).

All the molecular structures of dicupra[10]annulenes **2a−c** were confirmed by single-crystal X-ray structural analysis (for details see the Supporting Information (SI)). Here we discuss the structure of **2a** in detail as an example (Figure 2). The four Li
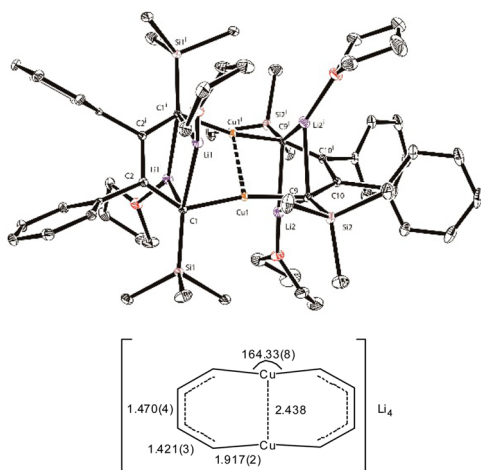

Figure 2. Molecular structure and selected bond lengths (Å) of dicupra[10]annulene **2a**. The ellipsoids represent a probability of 30%; H atoms are omitted for clarity reasons.

atoms, being coordinated with one THF molecule each, are located above and below the annulene ring. In comparison with bond lengths in dilithio reagent **1a** (1.533(2) Å and 1.367(2) Å, respectively), the C−C bond lengths within the annulene ring are remarkably averaged (1.470(4) Å and 1.421(3) Å, respectively), indicating considerable π-conjugation. The Cu−C bond length in **2a** is 1.917(2) Å, which is comparable with the classic Cu−C(sp^2) bonds (e.g., Cu−C bond length in CuC_6H_3-2,6-Trip$_2$, 1.894 Å).[9] The nearly linear C−Cu−C angle [164.33(8)°] suggests that the Cu atoms in **2a** are sp hybridized.

Figure 3 shows the single-crystal X-ray structure of **3a** (R = Ph). The two Li atoms, being coordinated with one THF molecule each, are located on the same side of the ring skeleton. In comparison with bond lengths in **2a** (1.470(4) Å and 1.421(3) Å, respectively), the C−C bond lengths in **3a** within the ring show clear 1,3-diene character with bond alternation (1.518(10)
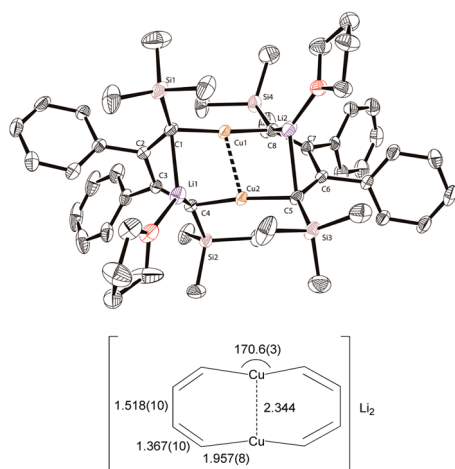

Figure 3. Molecular structure and selected bond lengths (Å) of dicupra[10]annulene **3a**. The ellipsoids represent a probability of 30%; H atoms are omitted for clarity reason.

Å and 1.367(10) Å, respectively). The Cu−C(sp^2) bond length in **3a** is 1.957(8) Å, slightly longer than that in **2a**. The C−Cu−C angle [170.6(3)°] is nearly linear, suggesting that the Cu atoms in **3a** should also be sp hybridized.

The dihedral angle between the two 1,3-diene planes for **2a** and **3a** is 35.7° and 77.8°, respectively. The distance between the two Cu atoms in **2a** and **3a** is 2.438 and 2.344 Å, respectively. The Natural Bond Orbital (NBO) analysis was then carried out to measure the Cu−Cu interaction. The Wiberg bond index of the Cu−Cu bond in **2a** and **3a** is 0.59 and 0.45, respectively, indicating a weak interaction between the two Cu atoms.[10]

To confirm the valence of the Cu atoms in **2**, XPS measurement was then carried out. The XPS data of **2b** detected the Cu 2p$_{1/2}$ and 2p$_{3/2}$ binding energies at 952.7 and 932.9 eV, respectively. The absence of Cu 2p$_{3/2}$ satellite peaks around 942 eV suggested that the Cu atoms in **2b** were not Cu(II) species. In consideration of the Cu LMM kinetic energy (915.8 eV), the Cu atoms in **2b** were more likely to be Cu(I) species,[11] which corresponds well with the sp hybridization hypothesis.

To further confirm and measure the aromaticity of dicupra[10]annulene **2**, ^{7}Li NMR was carried out in d^8-THF solvent with 0.1 M LiCl in d^8-THF as the external standard. The signal attributable to **2a** was found at −5.09 ppm (−6.04 ppm for **2b** and −6.17 ppm for **2c**). This low-frequency resonance was evidently caused by the strong shielding effect of the diatropic ring current, clearly showing the aromatic nature of dicupra[10]-annulenes. In contrast, the Li atoms in **3a** have a singlet only at δ = −1.04 ppm in d^8-THF. All these results suggest that dicupra[10]annulenes **2** did regain aromaticity when the two internal C−H moieties of [10]annulene are replaced with Cu atoms.

The isomerization stabilization energy (ISE) method of Schleyer and Pühlhofer is a general way to measure aromaticity.[12a] As shown in Scheme 2, the ISE reactions

Scheme 2. ISE Evaluations of Aromaticity of Dicupra[10]annulene 2b and Naphthalene (kcal/mol)
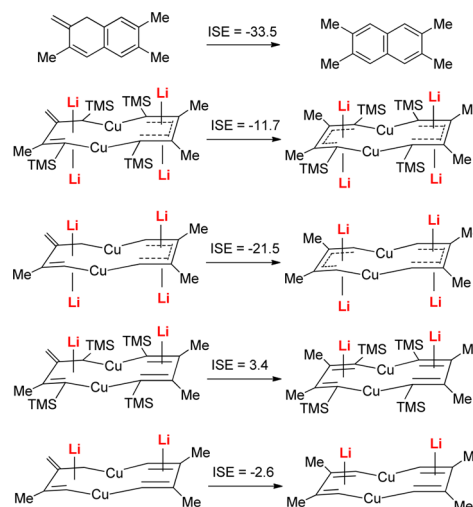
presented retained the same degree of unsaturation in the reactants and products. To exclude the effect of the sterically encumbered substituents, and to see the structure of genuine macrocycle, the theoretical calculations without TMS substituted analogues were also performed.[12b] The negative energies, −21.5 and −33.5 kcal/mol respectively, of the dicupra[10]annulene **2b** analogue and corresponding naphthalene demonstrated and

quantified their aromaticity. In comparison, the small negative ISE of the **3b** analogue (−2.6 kcal/mol) suggested that it is almost nonaromatic. These results also indicated that the twisted macrocyclic framework of **2** was partly due to the sterically encumbered TMS group and the framework itself should be aromatic.

Another useful tool to measure the extent of aromaticity is the nucleus-independent chemical shift (NICS).[13] The large negative NICS values (for the half ring of **2b**, NICS(0): −9.0, NICS(1): −9.8; for the half ring of **2b** analogue without TMS group, NICS(0): −12.8, NICS(1): −12.7) indicate its considerable aromaticity, which is consistent with experimental results (for more details, see STable 5 in the SI).

To gain more insight into the structure and electronic states of dicupra[10]annulene, density functional theory (DFT) calculations were carried out using Gaussian 09.[14] Structures of the dicupra[10]annulene **2b** without coordinated THF and its analogues were optimized at the B3PW91 level.[15] The 6-31G* basis set was used for C, H, Si, and Li atoms, whereas the LANL2DZ basis set was used for Cu atoms. The optimized geometry without THF was consistent with the X-ray data. Based on the optimized structure, NMR data were calculated using gauge-independent atomic orbital (GIAO) computations with a high basis set level.[16] The geometry structure of **2b** and its tetra-anion analogue (without Li atoms) are significantly different, indicating the noninnocent role of Li atoms which are more profound than just being part of an ion pair (Figure 4). Detailed results are given in the SI.
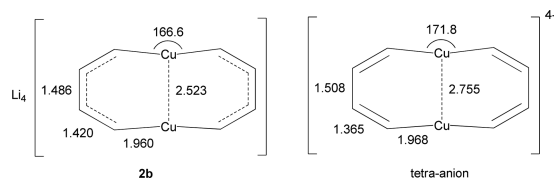

Figure 4. Optimized structures based on DFT calculations: **2b** (left) and its tetra-anion analogue (right).

The reaction mechanism for the formation of aromatic dicupra[10]annulenes **2** from dilithio reagents **1** and copper salts is intriguing and not clear yet. Based on our previous findings[8,17] and known reaction chemistry between organolithium and copper salts, a proposed reaction mechanism is given in Scheme 3. First, a transmetalation reaction between **1** and a Cu salt would afford butadienyl organocopper(I) aggregate **4**.[17] Formation of byproducts **3** at this stage is reasonable. The aggregate **4** would be regarded as a Cu-cluster, which can offer

**Scheme 3. Proposed Mechanism for the Formation of Dicupra[10]annulenes 2**
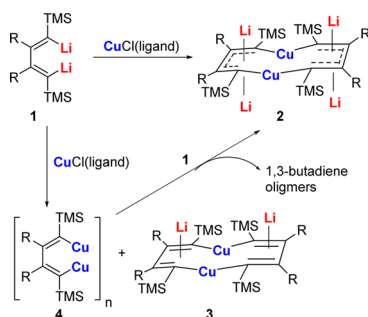
Cu and release homocoupling oligomers during reactions. The Cu-cluster **4** generated *in situ* would then react with **1** to form dicupra[10]annulenes **2** as the final products (together with cyclooctatetraene derivatives and octatetraene derivatives as other products, detected by MS spectroscopy). The dilithio reagent **1** behaved as a noninnocent ligand at the final step to form the aromatic dicupra[10]annulenes.[8] However, when we tried other Cu sources to react with diltho compounds **1** (such as active Cu power, Cu hydride clusters), no expected dicupra[10]-annulenes **2** could be detected by ^{7}Li NMR. Thus, detailed investigation is needed to elucidate the reaction process, especially the role of butadiene skeletons.

Compound **3** is also interesting and represents a new class of macrocyclic metallacycles. Inspired by the reported reaction chemistry of organocopper compounds,[18] we treated the dilithio reagent **1a** with mesitylcopper in a mixed solvent of hexane and diethyl ether at rt (Scheme 4). The reaction of **1a** with 2 equiv of

Scheme 4. Synthesis of 3a and 2a from Other Method
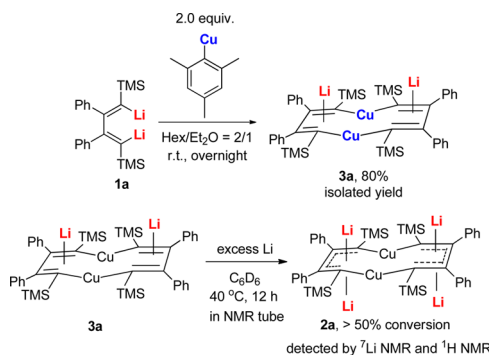
mesitylcopper proceeded smoothly, affording **3a** in 80% isolated yield. The reaction of **3a** with Li metal was then carried out. As shown in Scheme 4, **3a** could be converted into the corresponding dicupra[10]annulene **2a** in the NMR tube with an excess amount of Li metal, together with other unidentified products.

The XPS measurement of **3a** was also carried out. The Cu $2p_{3/2}$ binding energy and kinetic energy were at 933.2 and 914.6 eV, respectively. These results indicated **3a** was a typical Cu(I) species,[11] corresponding well with experimental data.

The recently developed adaptive natural density partitioning (AdNDP) method is useful and reliable for gaining theoretical insight into the nature of the delocalized bonding.[19] Thus, the AdNDP analysis of **2b** was then carried out using Multiwfn (for calculation details, see the SI).[20] The orbitals and occupation numbers (ON) are shown in Figure 5. AdNDP suggests that there are two delocalized 8c-2e π-bonds for each half ring of **2b**, together with one 14c-2e delocalized bonds. The contributions of main atoms of these AdNDP orbitals are given in the SI as STable 6.[21] Thus, the dicupra[10]annulene could be regarded as a 10 π-system.

In conclusion, we have synthesized, isolated, and structurally characterized the first series of aromatic dicupra[10]annulenes **2**. Unique structural characteristics and bonding models were revealed. This work provides a powerful protocol to construct macrocyclic metalla-aromatics and a good opportunity to further investigate metal-containing aromatics.
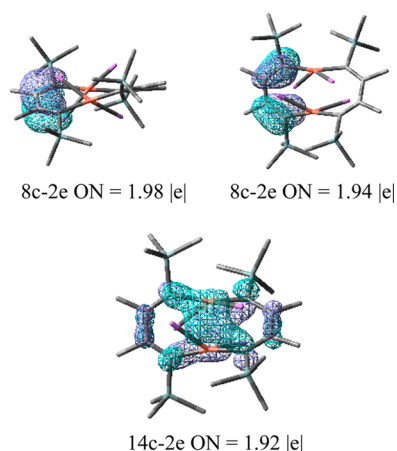
8c-2e ON = 1.98 |e|　　　8c-2e ON = 1.94 |e|

14c-2e ON = 1.92 |e|

Figure 5. Results of AdNDP delocalization. Isovalue = 0.04. The other two corresponding 8c-2e bonds are not shown.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11317.

　　Experimental details; calculation details; X-ray data for **2a**, **2b**, **2c**, **3a**; and NMR spectra of new products (PDF)
　　Crystallographic data (CIF)

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Notes
The authors declare no competing financial interest.

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