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Isolated Monomeric and Dimeric Mixed Diorganocuprates Based on the Size-Controllable Bulky "Rind" Ligands

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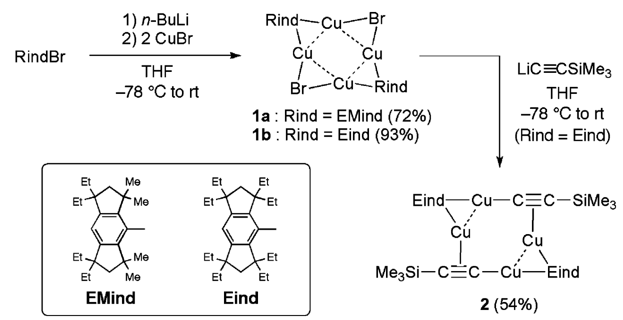
Organocopper compounds have been among the most widely used and powerful tools in synthetic organic chemistry;[1] these include organocopper(I) oligomers (CuR)$_n$[2] and a large variety of organocuprates such as diorganocuprates MCuR$_2$[3] and hetero-organocuprates MCuRX.[4] The structural elucidation of the actual species of organocopper reagents has met with difficulties because of their continuous aggregation−dissociation processes in solution.[5] For example, mixed diorganocuprates MCuRR′, which were introduced mainly on the basis of the so-called "dummy ligand" concept[6] and for selective ligand cross-coupling on copper,[7] generally come to equilibrium with two homoleptic species MCuR$_2$ and MCuR′$_2$ in solution, which sometimes causes undesirable side reactions. Thermally stable mixed diorganocuprates are quite rare.[3b,e,4] In this paper, we present the selective synthesis and isolation of monomeric and dimeric mixed diorganocuprates by introduction of the size-controllable "Rind" ligands based on a rigid fused-ring *s*-hydrindacenyl skeleton (Schemes 1 and 2), which we have recently developed[8] by the modified Kennedy's method.[9] The new bulky Rind groups have several advantages such as ease of preparation, high chemical stability, and size-controllability of steric bulkiness by the proximate substituents.

RindLi (Rind = EMind and Eind), which had been prepared from RindBr, was allowed to react with CuBr to afford neutral tetranuclear Cu(I) complexes **1** with a 2:1 Cu/Rind ratio (Scheme 1). Although we examined this reaction with various RindLi/CuBr molar ratios, no other organocopper species except **1** were observed because of the steric hindrance of the Rind ligands. Complexes **1** were isolated as air- and moisture-sensitive colorless crystals, and the molecular structure of **1b** was determined by X-ray analysis (Figure 1a). The four copper atoms form a planar and nearly rectangular structure alternately bridged by a bromine atom and a C$_{ipso}$ atom of the Eind ligand. The side Cu−Cu distances, 2.4274(10) and 2.7080(10) Å, are indicative of d^{10} metal−metal interactions.[10] The perpendicularly bridged Eind ligands are linked to the two Cu atoms in a symmetrical three-center−two-electron (3c−2e) bonding mode[2] with C$_{ipso}$−Cu distances of 2.000(4) and 1.981(4) Å. While compounds **1** are among the well-characterized RCu/CuX aggregated species,[11] **1** can also be regarded as the net dimer of two organohalocuprate [RindCuBr]$^-$ units sharing two Cu(I) ions.

In fact, the bromine atoms in **1** can be replaced by organic groups to form a net dimer of a mixed diorganocuprate sharing two Cu(I) ions, as shown in Scheme 1. Thus, the reaction of **1b** with lithium trimethylsilylacetylide gave **2** as pale-yellow crystals in 54% yield. According to the X-ray diffraction studies (Figure 1b), the long Cu−Cu distances in the planar Cu$_4$ core are further extended to 2.9041(5) Å by the ligand substitution, keeping the bridged Rind/Cu$_2$ core intact. Each alkynyl group is linked to the two Cu atoms through a short σ bond [Cu1−C29 = 1.878(2) Å] and a longer π coordination [Cu2−C29 = 2.013(2) and Cu2−C30 = 2.144(2) Å], thus adopting the rare case of the μ_2-η^1,η^2 bridging mode.[12] The C≡C bond [1.236(3) Å] is slightly elongated in comparison to a normal triple bond (1.20 Å); accordingly, the IR spectrum of **2** exhibits a ν(C≡C) stretching band at 1955 cm^{-1}, which is lower than that of Me$_3$SiC≡CH (2036 cm^{-1}).

Scheme 1



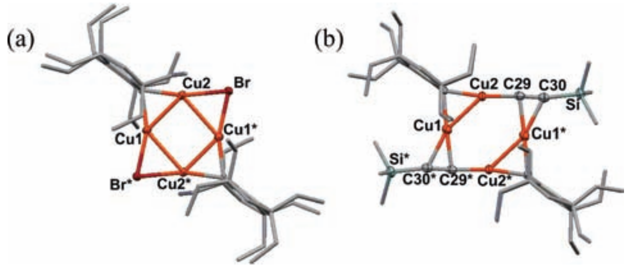


Figure 1. Molecular structures of (a) **1b** and (b) **2**. Hydrogen atoms have been omitted for clarity.

The copper clusters **1b** and **2** represent new members of the luminescent d^{10} clusters.[10] Thus, complex **1b** shows a weak green emission in the solid state with an emission maximum (λ_{em}) at 513 nm and a quantum yield (Φ) of 0.03, which might be attributed to an admixture of halogen to metal charge-transfer (XMCT) bromide → Cu$_4$ and metal-centered (MC) 3d → 4s/p transitions.[10] No detectable emission was observed in hexane or benzene, suggesting a weakened Cu−Cu interaction in solution. In contrast, complex **2** exhibits a strong orange emission in both the solid state (λ_{em} = 613 nm, Φ = 0.28) and solution (λ_{em} = 605 nm, Φ = 0.50 in hexane). The tetranuclear structure of **2** found in the crystal appears to be maintained even in solution because of the unique coordination of the alkynyl ligands, resulting in the efficient luminescence of the π(alkynyl) → 4s/p(Cu) transition with LMCT character.[10b,13]

Treatment of the much bulkier RindLi (Rind = MPhind and M^{s}Fluind) with CuBr exclusively produced monomeric organobromocuprates **3** with a 1:1 Cu/Rind ratio (Scheme 2). Figure

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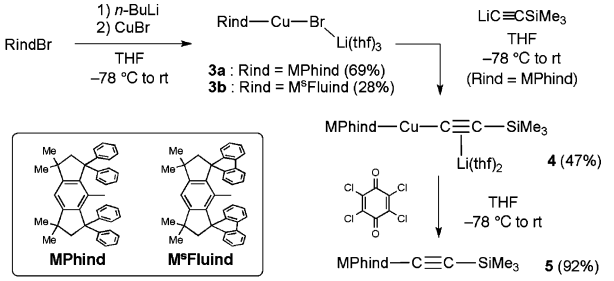
Scheme 2



2a shows the monomer structure of **3a**, where the lithium atom closely interacts with the bromine atom and three THF molecules. The copper atom has a linear two-coordinate geometry with a C−Cu−Br angle of 177.34(11)°. The relatively short C_{ipso}−Cu length [1.916(4) Å] lies in the range of those for 2c−2e σ-bonded arylcopper species.[2,3]

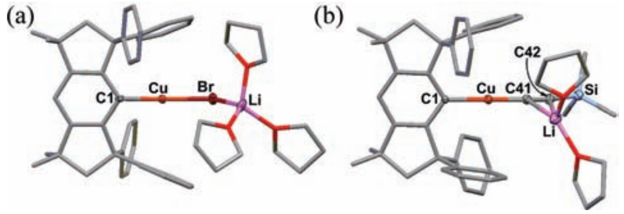


Figure 2. Molecular structures of (a) **3a** and (b) **4**. Hydrogen atoms have been omitted for clarity.

The subsequent reaction of **3a** with LiC≡CSiMe$_3$ produced the lithium aryl(alkynyl)cuprate **4** as colorless crystals containing two molecules of THF in 47% yield. Figure 2b shows its discrete monomeric nature, with the formation of a contact ion pair in which the lithium atom is bonded to the two carbon atoms of the acetylene unit. The geometry around the copper atom is slightly bent, having a C−Cu−C angle of 165.40(11)°, probably as a result of steric repulsion between the phenyl groups on the MPhind and the coordinated THF molecules. The Cu−C(sp^2) distance [1.942(2) Å] is longer than that of Cu−C(sp) [1.871(3) Å]. The C≡C distance is 1.222(4) Å, and the ν(C≡C) stretching vibration is observed at 1945 cm^{-1}, which is comparable to that of **2**. The mixed diorganocuprate **4** was found to undergo the oxidative ligand-coupling reaction[7] by the action of chloranil[7d] to selectively afford the bulky alkyne **5**. This provides direct experimental evidence for oxidative cross-coupling via the mixed diorganocuptrate arising from two different organolithium or magnesium reagents.

We have shown that the size-controllable Rind ligands can be used to generate isolable mixed diorganocuprates. In particular, while the chemical formula of MCuRR′ is generally accepted in organocopper chemistry, complex **4**, which was realized by the significant bulkiness of the MPhind group, represents to the best of our knowledge the first isolable monomeric mixed diorganocuprate.

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Supporting Information Available: Experimental details and crystallographic data (CIF). This material is available free of charge via Internet at http://pubs.acs.org.

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