Review

C,C- and C,N-Chelated Organocopper Compounds†

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† Dedicated to Professor Gerard van Koten on the occasion of his 80th birthday

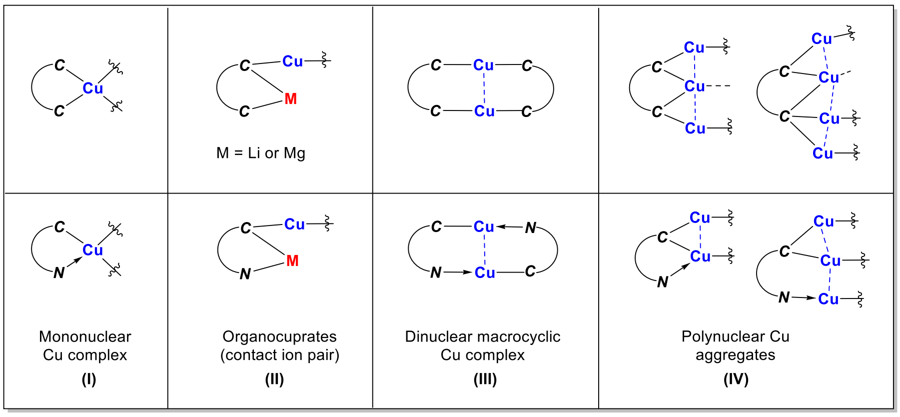
Abstract: Copper-catalyzed and organocopper-involved reactions are of great significance in organic synthesis. To have a deep understanding of the reaction mechanisms, the structural characterizations of organocopper intermediates become indispensable. Meanwhile, the structure-function relationship of organocopper compounds would advance rational design and development of new Cu-based reactions and organocopper reagents. Compared to the mono-carbonic ligand, the C,N- and C,C-bidentate ligands better stabilize the unstable organocopper compounds. The bidentate ligands can chelate to the same copper atom via η^2-mode, forming a mono-cupra-cyclic compounds with at least one acute C-Cu-C angle. When the bidentate ligands bind to two copper atoms via η^1-mode at each coordinating site, the bimetallic macrocyclic compounds will form nearly linear C-Cu-C angles. The anionic coordinating sites of the bidentate ligand can also bridge two metals via μ_2-mode, forming organocopper aggregates with Cu-Cu interactions and organocuprates with contact ion pair structures. The reaction chemistry of some selected organocopper compounds is highlighted, showing their unique structure-reactivity relationships.

Keywords: organocopper; C,N-chelated; C,C-chelated; bidentate; butadienyl; intramolecular coordination; three center-two electron bonds; structure-reactivity relationship

1. Introduction

Copper-mediated or -catalyzed reactions have been upgrading the toolbox of organic synthesis with a variety of cheap, efficient transformations, which benefit scientific research in a broad range of areas, such as polymer chemistry and biochemistry[1-12]. To have a deep understanding of the reaction mechanisms, organocopper species, as proposed intermediates, are sought to be isolated. On the other hand, organocopper compounds can be easily prepared *in situ* and utilized as organometallic synthons to construct various small organic molecules[13-15]. A well-recognized example is that "hard" nucleophiles, e.g., organolithium or Grignard reagents, react with *α*,β-unsaturated carbonyl compounds via 1,2-addition, whereas the "soft" organocuprates will end up with 1,4-addition products with the same substrates[16,17]. In a catalytic version, in the presence of copper salts, Grignard reagents can behave similarly to the organocuprates[18]. It is known that reactivities are closely connected to structural configurations. The organocopper chemistry focused on establishing the structure-reactivity relationship of well-defined organocopper compounds, rationalizing the unlike reaction patterns of different organometallic copper reagents.

Transmetalation provides the most straightforward and reliable method to prepare organocopper compounds from readily available organometallic reagents[19,20], though many other synthetic strategies were also known, such as copper-halide exchange reaction[21], direct cupration[22], and oxidative addition of reactive Rieke Cu*[23]. It should be emphasized that the identity of forming organocopper compounds is very much dependent on the ratio of starting materials. For example, in the early 19th century, Gilman and et al. found that the reaction of methyl lithium and 1.0 equiv. of copper(I) salts formed insoluble methylcopper polymers as yellow solids in diethyl ether[24]. When 0.5 equiv. of copper(I) salts was used in the above condition, a clear solution of dimethyl cuprate (Gilman reagent) was afforded. Initial isolation and characterizations of organocopper compounds were very slow, since the reactive species are subject to thermally homolytic, oxidative, and hydrolytic decompositions[25]. A general trend is the stability increases from alkyl, alkenyl, aryl to alkynyl copper compounds. For example, methylcopper[24] and phenylcopper[26] clusters display rapid and slow decompositions at room temperature, respectively, while (phenylethynyl)copper[27] looks stable under ambient conditions. The stability trend could also be reflected by the numbers of single-crystal structures in the Cambridge Structural Database (CSD 5.42, 2020 November), in which roughly 185 alkyl, 288 aryl, and 326 alkynyl copper compounds were collected. Moreover, the aggregate state, which is favorable in charge-neutral organocopper compounds, makes these polymeric compounds poorly soluble in common organic solvents. To solve the above inherent problems of organocopper compounds, coordinating heteroatom-containing moieties, such as dimethyl amino groups, are rationally introduced in the ligand skeleton by van Koten and others to enhance the stability and solubility[28,29]. The hybrid C,N-bidentate ligands can bind to copper atoms with an enhanced chelating effect. In a different path, Xi group discovered that 1,4-dilithio 1,3-butadienes (C,C-bidentate ligand) can stabilize reactive organocopper species in a great extent via a cooperative effect[30,31]. In addition, this C,C-bidentate ligand can also be regarded as an analogue of 1,2-diketimine, which turns out to be a special Z-type non-innocent ligand, affording an unprecedented aromatic dicupro-annulenes[32].



Scheme 1. Fragments in the molecular structures with characteristic connectivity. The lines do not necessarily represent 2c-2e or 3c-2e bonds.

Here in this review, we're interested in summarizing organocopper compounds with at least one Cu-C σ-bond, in which the organic fragments behave as actor ligands rather than spectator ligands (e.g., Cp, NHC). For mono-dentate carbonic ligands, the binding between copper and carbon atoms normally consists of the regular two-center two-electron (2c-2e) σ-bonds and three-center two-electron (3c-2e) bonds[33] when the carbon atom bridges two copper atoms. In the case that the bridging carbon atom is linked with a copper and a lithium (or magnesium) atom, the binding is more likely between 2c-2e and 3c-2e bonds. For neutral nitrogen-containing groups, the binding of Cu-N is a traditional dative bond. When extending from one coordinating site to C,N- or C,C-chelating ligands, the binding in the corresponding organocopper compounds becomes more diverse. Based on the *characteristic connectivity* of fragments in the structures, the

C,N- and C,C-chelated organocopper compounds can be put into the following four categories:

1) Mononuclear organocopper complexes

The two coordinating sites of C,C- and C,N-bidentate ligand bind to the same Cu center together, forming a 5-membered chelate ring as shown in **(I)** of Scheme 1. The two chelate rings connected with a copper atom will generate a spiro complex.

2) Organocuprates with contact ion pair structures

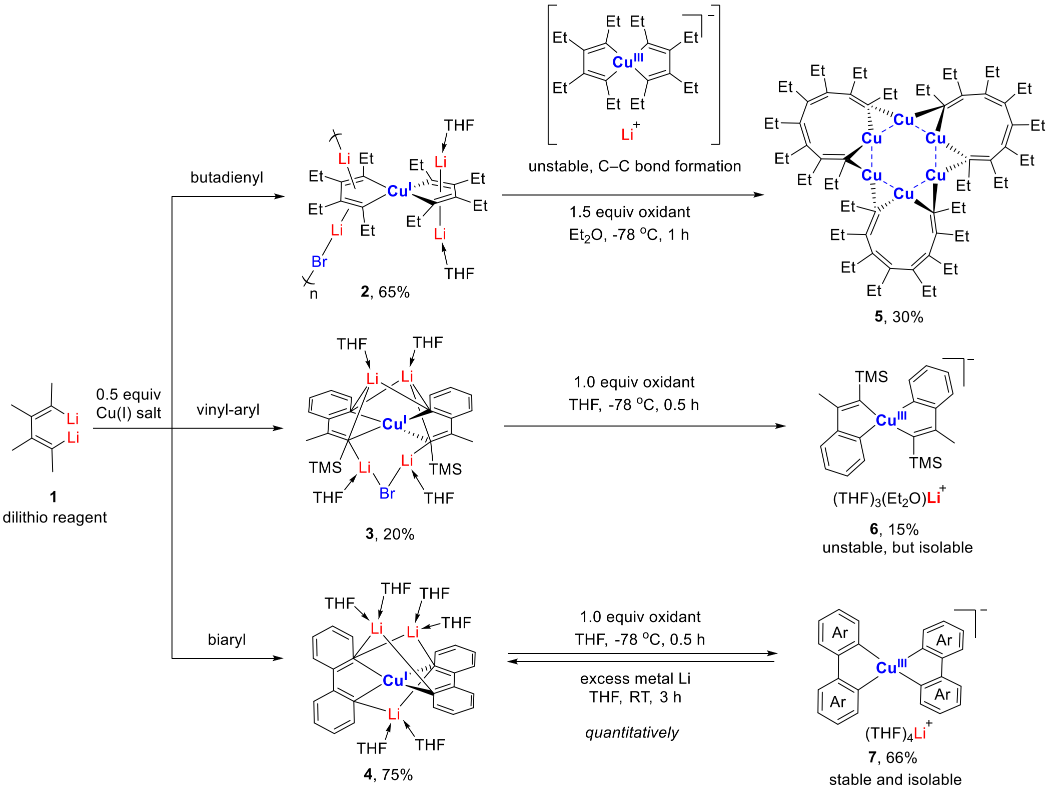
The two coordinating sites can be attached with different metals, with one site bound to the Cu/M atoms and the other one bound to the main group metal atoms M only. The resulting product can be regarded as organocuprates with contact ion pair structures **(II)**.

3) Binuclear macrocyclic copper complexes

Each coordinating site of C,C- and C,N-bidentate ligand can also bind an individual Cu atom with 2c-2e bonds, forming a macrocyclic dinuclear complex. As a result, each Cu atom forms a linear geometry with two units of bidentate ligands that provide only one coordinating site to each Cu atom **(III)**.

4) Polynuclear organocopper aggregates

If the carbanion bridges two copper atoms, the structural feature will likely be polynuclear copper aggregates with Cu-Cu interactions **(IV)**.

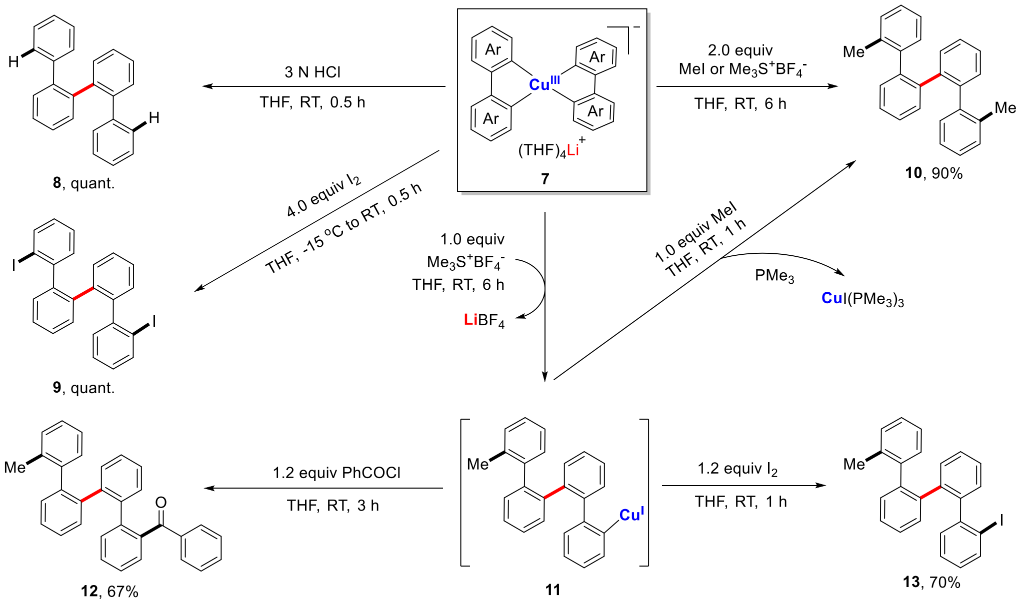


Scheme 2. Organometallic spiro copper(I) and Cu(III) complexes.

2. Mononuclear organocopper complexes

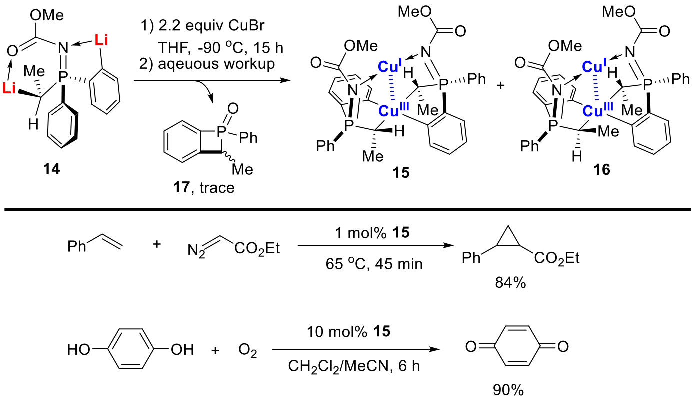
Although neutral N,N-chelated spiro copper complexes are relatively common, the anionic C,N- or C,C-cheated spiro counterparts are sporadic. As mentioned above, Xi group found that the C,C-bidentate ligand is an excellent platform to build up diversified coordination complexes across the periodic table[32,34-60]. The chelating effect increases the thermal stability of these organometallic species, facilitating the isolation and following characterization. And their metal-carbon bonds remain reactive toward electrophiles. As a result, a good balance between stability and reactivity is achieved.

Starting from the 1,4-dilithio 1,3-butadienes **1** (dilithio reagent for short) and 0.5 equiv. of copper(I) salts, Xi group isolated the first series of spiro organocopper(I) compounds **2**-**4** (Scheme 2)[59,60]. It seems that the terminal alkenyl carbon atom is favorable for LiBr coordination, probably because it is more electron-rich than the phenyl ones. The butadienyl spiro copper complex **2** formed one-dimensional polymers with repeating units linked by Li—Br. When one vinyl moiety was replaced by a phenyl ring, LiBr forms a Li_2Br fragment between two vinyl carbon atoms of **3**. No LiBr salt was found in the biphenyl spiro copper complex **4**. The copper atoms are all coordinated with two dianionic ligands, forming a distorted tetrahedral geometry (dihedral angels between two five-membered chelate rings is about 63-84°). Averaged Cu(I)-C bond lengths of **2**-**4** are from 2.01 to 2.06 Å. Upon oxidation, either the dianionic ligand or the metal center can be oxidized depending on the electron-richness of the ligands. **1** was transformed to a hexanuclear tetraenyl copper cluster **5** with a Cu_6 hexagon. In this process, the oxidative dimerization of the original butadienyl ligand occurred. It might undergo a spiro Cu(III) intermediate, which was too unstable to be isolated. When **3** was treated with oxidizing agents, a spiro Cu(III) complex **6** was afforded and isolated successfully. **6** is thermally unstable and difficult to handle at room temperature. With an extended conjugated backbone, **4** was oxidized to form a very stable spiro Cu(III) complex **7**. In addition, **7** can be reduced by metal lithium to regenerate **4** quantitatively. Both **6** and **7** have copper atoms with a distorted square planar geometry. Averaged Cu(III)-C bonds of **6** and **7** (1.96-1.97 Å) are noticeably shorter than Cu(I)-C bonds of **2**-**4**. It is noteworthy that **6** and **7** represent a novel type of unprecedented organocopper(III) complexes. By virtue of Cu $L_{2,3}$-edge X-ray absorption spectroscopy and experimentally calibrated electronic structure calculations, Lancaster and co-workers found that the Cu(III) complex **7** has a LUMO (lowest unoccupied molecular orbital) with only ~25% Cu 3d character, which suggests the formal Cu(III) is not a physical d^8 configuration[61].



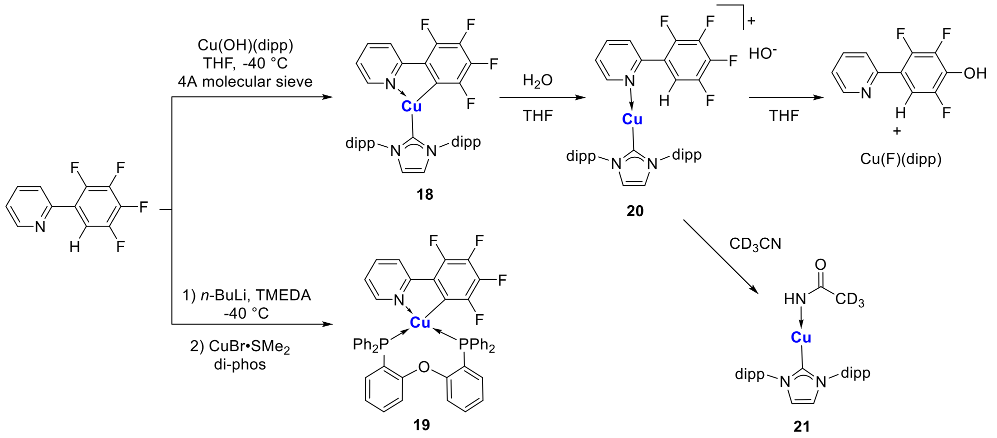
Scheme 3. Reductive elimination of organometallic spiro Cu(III) complexes.

As revealed by the crystal structure of **7**, all four aryl rings are at *cis*-positions, which in principle provides a favorable arrangement for reductive elimination. However, no C-C bond formation occurred when the anionic compound **7** itself was reflux overnight. However, when treated with electrophiles, e.g., aqueous HCl solution, iodine, and alkylation reagents, **7** afforded the symmetrical quaterphenyl derivatives **8**-**10** facilely in almost quantitative yields via an electrophilic attack followed by a reduction elimination (Scheme 3). A stepwise experiment shows **7** reacted with 1.0 equiv. of methylation agent, producing a quaterphenylcopper(I) species **11**, which can couple with other electrophiles to form di-substituted quaterphenyl compound **10**, **12**, and **13** in high yields. Reductive elimination of high-valent copper compounds was often proposed as the final step to release the product, but there was nearly no concrete experimental evidence on that until this work.



Scheme 4. Mixed-valent bimetallic Cu(I)/Cu(III) compounds

In a similar vein, López-Ortiz and co-workers reported the reaction between dilithiated phosphazene **14** with 2.2 equiv. of CuBr followed by an aqueous workup to afford two diastereotopic isomers of mixed-valent Cu(I)/Cu(III) complexes **15** and **16** in 53% combined yield, in which the Cu(III) center was chelated with two C,C-bidentate aryl-alkyl ligand (Scheme 4)[62]. A byproduct with four-membered ring **17** was isolated too. Both **15** and **16** can be purified by column chromatography. Accordingly, they are stable in air and moisture. The Cu(III) and Cu(I) adopt a distorted square planar and linear geometry, respectively. Averaged Cu(III)-C bond (1.98 Å) in **15** and **16** is similar to that in **6** and **7**. The oxidation states of Cu ions in **15** were further confirmed by extended X-ray absorption fine structure (EXAFS). Furthermore, all the pieces of evidence, including the short Cu-Cu distance(2.74 Å) in the single-crystal structure, a bond critical point in the topological analysis of the X-ray experimental Fourier map, as well as a diagnostic absorption band at 343 nm, strongly supported a weak metal-metal d^8-d^{10} bonding between two Cu ions. **15** can be used as the catalyst in the catalytic cyclopropanation and aerobic oxidations. The characteristic signal of **15** was observed, which suggests that **15** remains unaffected during the transformations, probably due to its rigid structural configuration and extremely high stability.

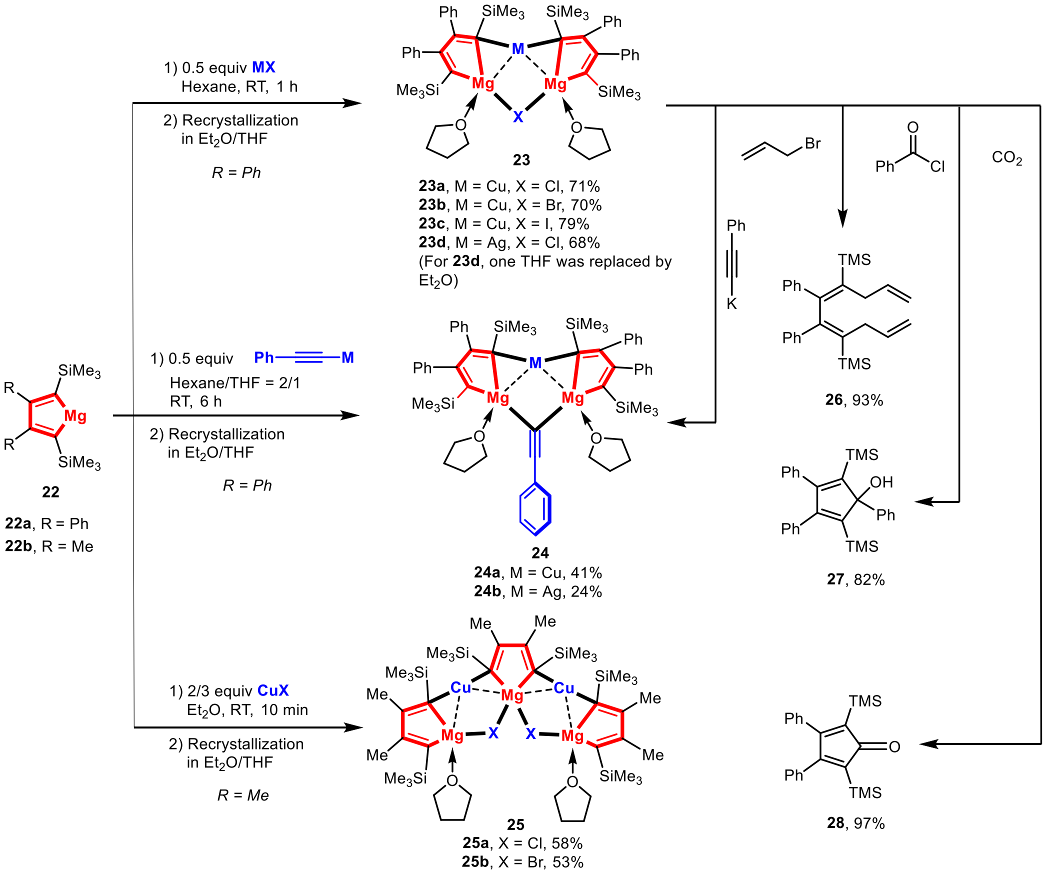


Scheme 5. C,N-chelated organocopper compounds

2-phenylpyridine and its derivatives are among the most popular scaffolds for photoactive transition metal complexes. Partial fluorination of the aryl ring makes the C-H bond at 2-position very acidic. And at the same time, it increases the stability of the resulting Cu-C bond. Steffen and co-workers reported that the C,N-chelated organocopper compound **18** was obtained from a direct metalation from Cu(OH)(NHC), in which 4A molecular sieves play an essential role to remove the water (Scheme 5)[63].

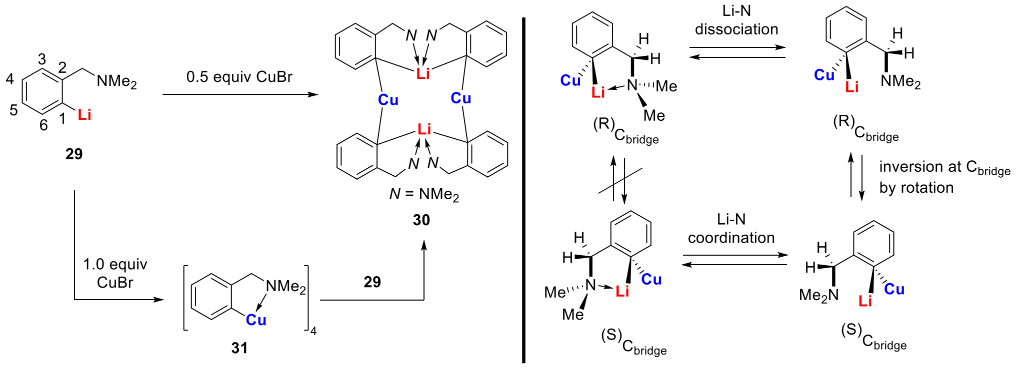
In the presence of water, compound **18** will inevitably undergo hydrolysis process, regenerating the C-H bond and forming the ionic species **20**. The counteranion of hydroxide in **20** will replace a fluoride at 4-position via a nucleophilic aromatic substitution in THF to 4-hydroxyl-2-arylpyridine and copper fluoride species. When MeCN was used as the solvent, hydroxide will attack MeCN, forming a copper acetamide species **21**. Similarly, a spiro complex **19** can also be prepared from lithiation and subsequent transmetalation with $CuBr\cdot SMe_2$ in the presence of diphosphine ligands. It is shown in the single-crystal structures that **18** and **19** adopt distorted trigonal and tetrahedral coordination geometries, respectively. In solution, **18** is weakly emissive. In the solid state, the C,N-chelated organocopper compounds exhibit intense orange-red luminescence (λ_{max} = 610 (**18**), 607 (**19**) nm) at room temperature, with phosphorescence lifetimes of τ = 8.6 (**18**) and 9.5 (**19**) μs).

3. Organocuprates with contact ion pair structures



Scheme 6. Rigid magnesium organocuprates

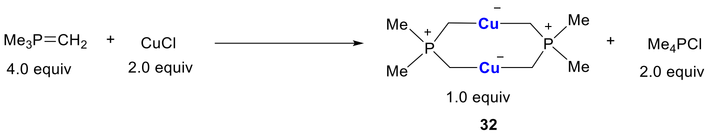
As mentioned in the Introduction, organocuprates have been extensively used in organic synthesis. Although numerous lithium organocuprates have been structurally characterized, the equally important magnesium organocuprates remain less unexplored, especially in terms of their well-defined structures. Only a few examples of aryl magnesium organocuprates were reported before[64]. As reported in the previous work of Xi and co-workers [35], magnesiacyclopentadienes **22**, the first alkaline-earth metallocyclopentadienes, have a small C-Mg-C bite angle and coplanar 5-membered chelate ring. The bridging character of anionic carbon atoms (Lewis base) and coordinative unsaturation of the Mg atom (Lewis acid) make **22** available to bind other metal salts. Two equiv. of **22** reacted with 1.0 equiv. of copper halides or (phenylethynyl)copper to afford magnesium organocuprates **23a-c** and **24a** with a Cu:Mg ratio of 1:2 (Scheme 6)[58]. In addition, the inert silver halides, as well as alkynyl silver compounds, can apply to the above transformations, giving magnesium organoargenates **23d** and **24b**. The structures of forming organocuprates are dependent on the substituents at 2,3-positions for some reason. When the substituents are changed from Ph to Me groups, **25** with a Cu:Mg ratio of 2:3 was obtained as the major products. Structural analysis and DFT calculation (AIM) revealed that as the Cu-C bonds form, a Mg-C bond becomes highly weak (2.34 Å), while the other one remains unchanged (2.11 Å) in **23a**. It seems that two Mg atoms provide a pre-organized position to anchor the halides. The C-Cu-C bond angle (157°), as well as the Cu-C bond lengths (1.95 Å), indicates a Cu-C-Mg 3c-2e bonding character. As supported by the molecular structure and DFT calculations, no bonding interaction was found between Cu-Br in **23a**. On the whole, the binding of anionic $C(sp^2)$ carbon atoms to the Cu atom and the bridging of Mg atoms by halides lead to a formal heterolytic cleavage of M-X bond (M = Cu, Ag; X = halide, alkynyl) in a cooperative way, along with the transfer of anionic X units from M centers to Mg centers. Accordingly, **23-25** can be considered as a resting-state intermediate of the transmetalation reaction between organomagnesium reagents and coinage-metal salts. The bridging ligand can be transformed quantitatively, e.g., **23c** → **23a** or **24a**. The preliminary reactivity of these rigid magnesium organocuprates was provided by the reactions of **23c** with various electrophiles, producing small organic molecules **26-28**.



Scheme 7. Neutral C,N-bidentate organocuprates

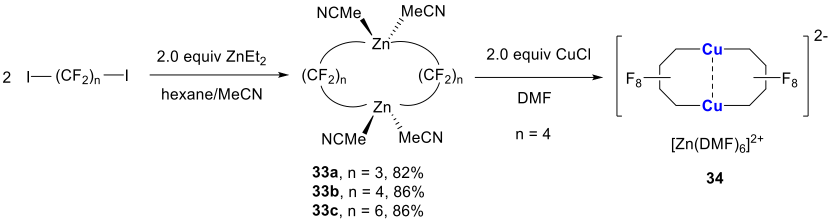
When a built-in coordinating site is added to the monoanionic phenyl skeleton at the *ortho*-position, it will generate a C,N-bidentate ligand, as shown in Scheme 7. With the (dimethylamino)methylphenyl (DMMP) lithium reagent **29** in hand, van Koten group developed two methods to synthesize the dicopper-dilithium organocuprate **30**: 1) a direct transmetalation of **29** with 0.5 equiv. of CuBr, 2) an interaggregate exchange reaction between DMMP copper cluster **31** (vide infra) and **29**[65,66]. The short averaged Cu-C bonds (1.94 Å) as well the weak averaged Li-C bonds (2.39 Å) in **30** suggest that Cu-C bonds have a higher character of 2c-2e bond[67]. However, the split coupling of ^{13}C-^{7}Li (7 Hz) was still observed in solution, which indicates the s electron density is present between the Li and C(*bridge*) nuclei[68]. Meanwhile, the J(^{13}C-^{7}Li) did not change during variable-temperature NMR studies, which could exclude the intraaggregate exchange processes. By monitoring the characteristic signals of methylene protons (AB pattern) and NMe_2 protons (two singlets) using dynamic ^{1}H and ^{13}C NMR spectroscopies, van koten and co-workers found the rotation of 3c-2e bonded aryl groups around the C(1)-C(4) axis for the first time[69]. The $C_4Cu_2Li_2$ core fragment appears to be a persistent structural feature in neutral aryl lithium organocuprate (contact ion structure[64]).

4. Binuclear macrocyclic copper complexes



Scheme 8. Cyclic alkyl dicopper complex

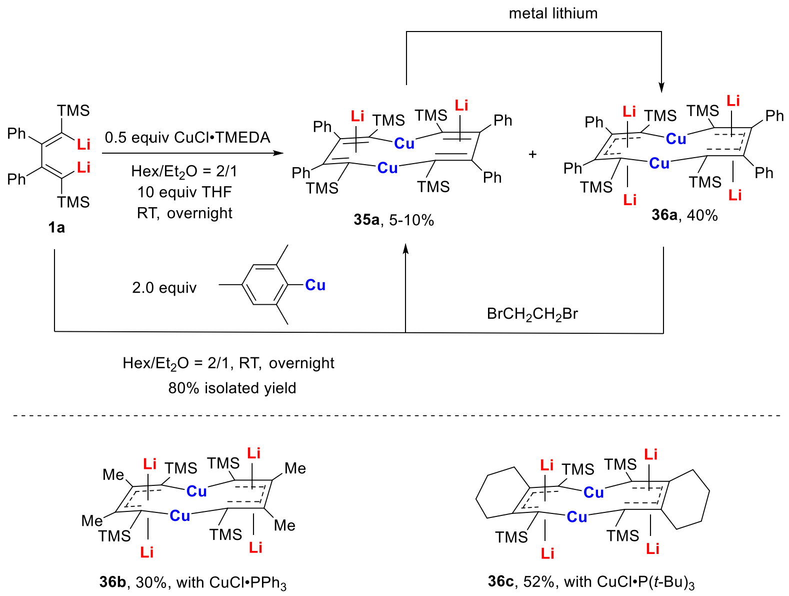
It seems that trimethylmethylenephosphorane ($Me_3P{=}CH_2$) shows a better stabilization effect on Cu-C bonds than its isoelectronic analogue $Me_3Si\text{-}CH_2$. Buchner and Zangrando found that treatment of $Me_3P{=}CH_2$ with CuCl afforded a binuclear cuprate complex **32**, in which negative charges are formally located at Cu atoms while positive charges are at phosphine atoms (Scheme 8)[70,71]. In this process, the hybridization of CH_2 was changed from sp^2 to sp^3. The core structure of $P_2(CH_2)_4Cu_2$ forms a coplanar 8-membered macrocycle. Averaged Cu-C bond (1.96 Å) and C-Cu-C bond angel (176°) are in the typical ranges of organocuprates.



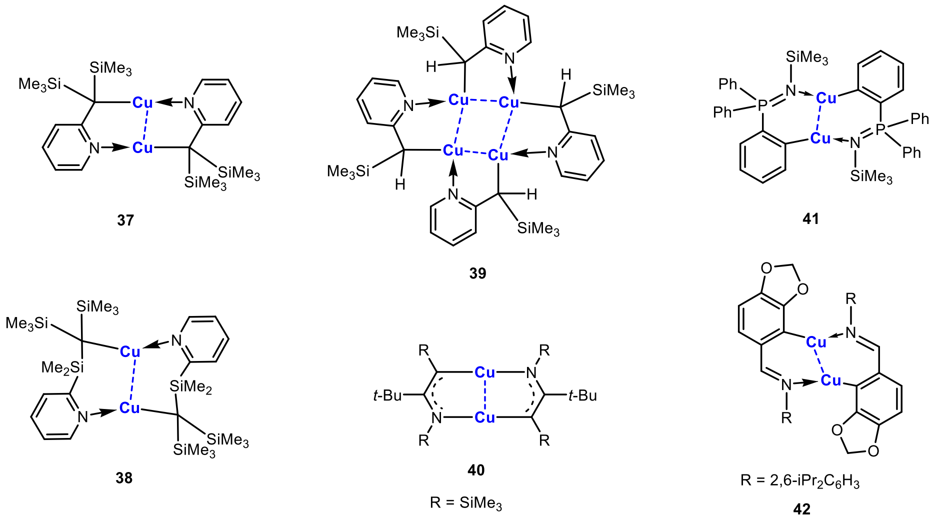
Scheme 9. Perfluoro-dicupra-cyclodecanes

Recently, there is an increasing interest in $(CF_2)_n$-containing materials in the industry. However, the methods to incorporate difluoromethylene in molecules are lagging behind other perfluroalkyl counterparts. Vicic and co-workers reported a new route to access perfluoroalkyl-based metallacycles with varied ring sizes (Scheme 9)[72]. Tetra-perfluoroalkyl-dizinc compounds **33** were obtained from the reaction of diiodoperfluoroalkanes with 2.0 equiv. of $ZnEt_2$. Treatment of **33b** with 2.0 equiv. of CuCl in DMF afforded a 10-membered dicopper compound **34**. The averaged Cu-C bond (1.93 Å) is relatively shorter than that of other non-fluorinated alkyl cuprates. **34** was inactive towards electrophiles, consistent with its strong Cu-C bond and high stability.

Metal-containing aromatic molecules have attracted much attention recently. Compared to the six-membered metallobezenes and metallabenzynes as well five-membered metallocylcopentadienes, the macrocyclic metalla-aromatics are less explored. *Trans*,*cis*,*trans*,*cis*,*cis*-[10]annulene is a conjugate molecule with 10-π electrons. However, it is non-aromatic, due to the steric repulsion between the two internal hydrogen atoms. It was envisioned that replacement of two internal CH with transition metal not only releases the steric hindrance, but also provides electrons to the delocalized π-system. Aromatic dicupra[10]annulenes **36** with four lithium atoms were first synthesized and isolated from the reaction of dilithio reagents **1** and CuCl complex by Xi group (Scheme 10)[32]. In the above reactions, **35** with two lithium atoms was isolated as the byproduct in a small amount, which can also be efficiently synthesized from dilithio reagent and mesitylcopper. More importantly, reversible two-electron transformations between **35** and **36** were observed[47]. Compared to the alternating bonds of butadienyl skeleton in **35a** (1.52, 1.37 Å), C-C bonds of annulene moiety in **36a** are remarkably averaged (1.47, 1.42 Å), suggesting a considerable π-delocalization. The Cu-C bonds of **36a** (1.92 Å) were notably shorter than those of **35a** (1.96 Å), which might be attributed to the extra two electrons posed to **36a**. The Cu 2p$_{3/2}$ binding energy (932.9 eV) and Cu LMM kinetic energy (915.8 eV) of **36b**, as displayed by XPS data, show that the Cu atoms in **36** are more like to be Cu(I). With assembled experimental results (the above crystallographic data; low-frequency resonance signals of ^{7}Li NMR: -5.1 to -6.2 ppm) and DFT calculations (negative values of ISE: -11.7 and -21.5; large negative NICS values: -9.0 to -12.8), it is safe to conclude that dicupra[10]annulenes are aromatic. AdNDP analysis suggested dicupra[10]annulenes could be regarded as a 10-π aromatic system. Based on independent theoretical calculations, Grande-Aztatzi and co-workers consider dicupra[10]annulenes as a metalla-naphthalene[73]. Zhu and co-workers suggest that dicupra[10]annulenes have 16e Craig-type Möbius aromaticity[74]. And both Zhu's and Sundholm's calculations reveal that lithium counterions play an important role in these organocopper complexes[74,75].



Scheme 10. Aromatic dicupra[10]annulenes

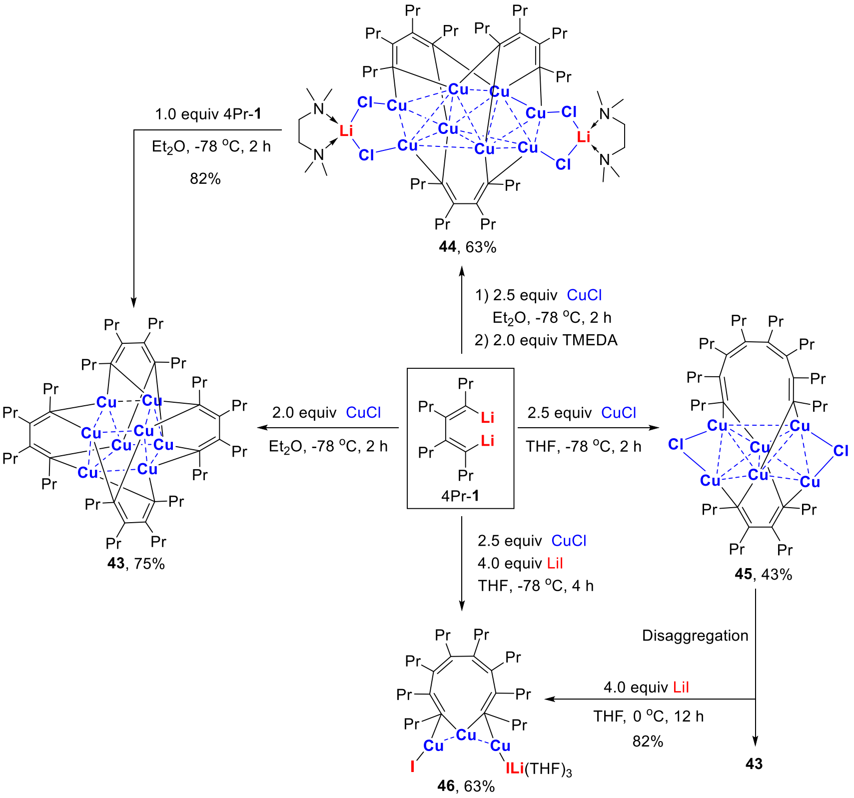


Scheme 11. C,N-chelated cyclic organocopper compounds

As shown in Scheme 11, C,N-chelated dicopper compounds **37**,**38** and **40-42** documented in the literature are generally macrocyclic neutral species, since the two negative charges of ligands are exactly balanced with two Cu(I) atoms[76-82]. An early example of structurally well-defined alkylcopper compounds was $[Me_3SiCH_2Cu]_4$, in which trimethylsilyl groups not only pose steric hindrance to increase the stability, but also improve the solubility by virtue of lipophilicity of silicon groups[83,84]. White and others found that incorporating an *ortho*-bulky bis-trimethylsilyl-alkyl ligand at a pyridine can stabilize the dicopper compound **37** to a great extent[76,80]. **37** can be sublimated at 160 ℃ without decomposition. **37** features an 8-membered core structure ($C_4N_2Cu_2$). When increasing the distance between the alkyl moiety and the pyridine, a dicopper compound

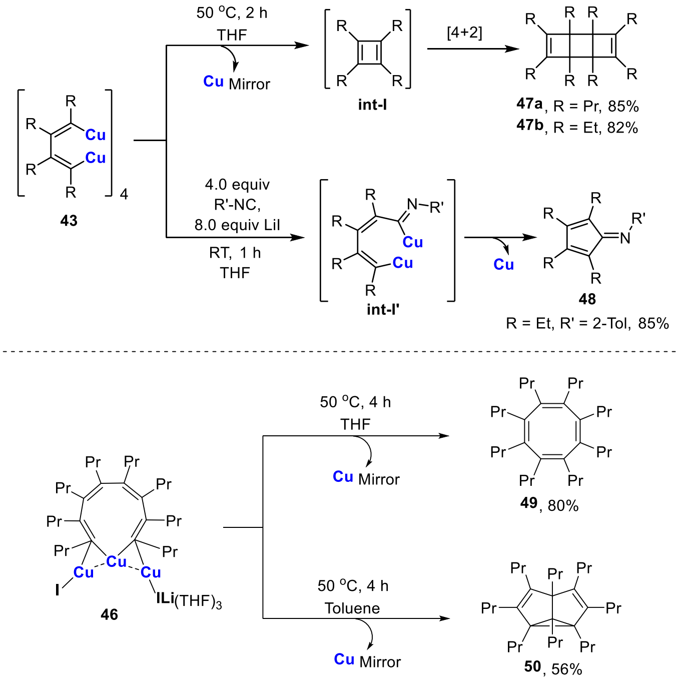
38 with a 10-membered ring can also be generated, as reported by Eaborn and Smith[81]. However, with a smaller steric effect, the alkyl-pyridine ligands will bind four copper atoms, generating a tetracopper complex **39**[77]. Similarly, three dicopper compounds **40**-**42** based on 1-azaallyl, aryl-phosphanimine, and aryl-imine ligands were synthesized from the corresponding lithiated starting materials and copper salts by Lappert[78], Stalke[79], and Schmidt[82], respectively. The Cu-C bonds of **37**-**40** are in the range of 1.93-1.95 Å, which suggests a mostly 2c-2e Cu-C bond, while the Cu-C bonds (1.91 Å) in **41** and **42** fall in the short end of the range observed for Cu-C 2c-2e bonds. Cyclic voltammetry and bulk electrolysis of **37** show very promising evidence of the existence of formal copper(II) alkyl species with relatively high stability.

5. Polynuclear organocopper clusters



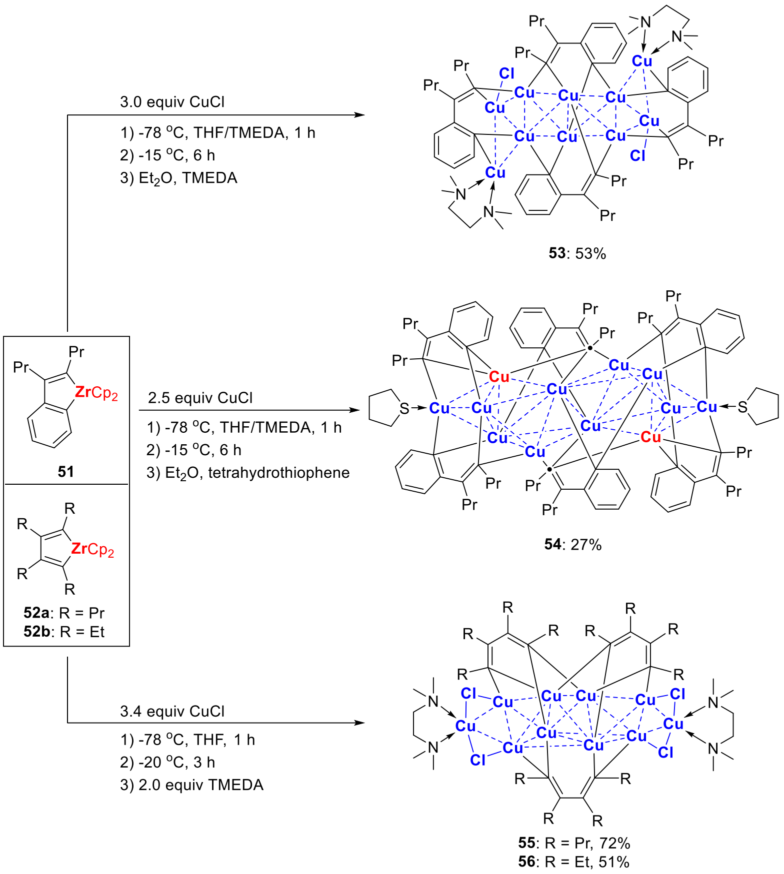
Scheme 12. Conjugate C,C-bidentate organocopper aggregates

Fifteen years ago, Xi and co-workers reported that the *cis*-1,3-butadienyl 1,4-dicopper species, obtained from the reaction of dilithio reagent with 2.0 equiv. of CuCl, produced multi-substituted semibullvalenes efficiently after thermolysis at 50 ℃ in the non-coordinating solvent of toluene[85]. Later on, it was found that the same copper species underwent lithium iodide-assisted linear dimerization in Et_2O at 0 ℃ to afford an all-*cis* octatetraenyl dicopper intermediate that could be subject to subsequent Pd-catalyzed cross-coupling reactions with halides[86]. In order to unveil the nature of butadienyl copper species, Xi and co-workers carefully carried out the transmetalation reactions at low temperature (-78 ℃) to avoid uncontrollable thermal decompositions. The reaction of dilithio reagents 4Pr-**1** with 2.0 equiv. of CuCl in Et_2O afforded 1,4-dicopper tetramer **43** in 75% yield (Scheme 12)[56]. When 2.5 equiv. of CuCl was used in the presence of 2.0 equiv. of TMEDA, a different copper aggregate **44** was obtained in 63% yield. **44** could be transformed to **43** by treatment with 1.0 equiv. of dilithio reagent. Additionally, the products were also dependent on the solvents and additives, e.g., lithium salts. When THF was used as the solvent, the reaction of dilithio reagent with 2.5 equiv. of CuCl afforded **45**, which was linked by a 1,3-butadienyl and a 1,3,5,7-octatetraenyl units in 43% yield. In the presence of extra LiI, the above reaction produced 1,3,5,7-octatetraenyl-1,8-dicopper compound **46** in 63% yield. 1,3,5,7-octatetraenyl unit was formed from the dimerization of butadienyl copper complexes, as observed in the previous work[86]. **46** and **43** can also be generated from the reaction of **45** and LiI. Structural analysis of **43**-**46** reveals that the Cu-C bonds and C-Cu-C bond angles are in the range of 1.96-2.08 Å and 73-84°, respectively. The close Cu-Cu distances (2.37-3.01 Å) suggests a weak d^{10}-d^{10} interactions in all the copper aggregates above.



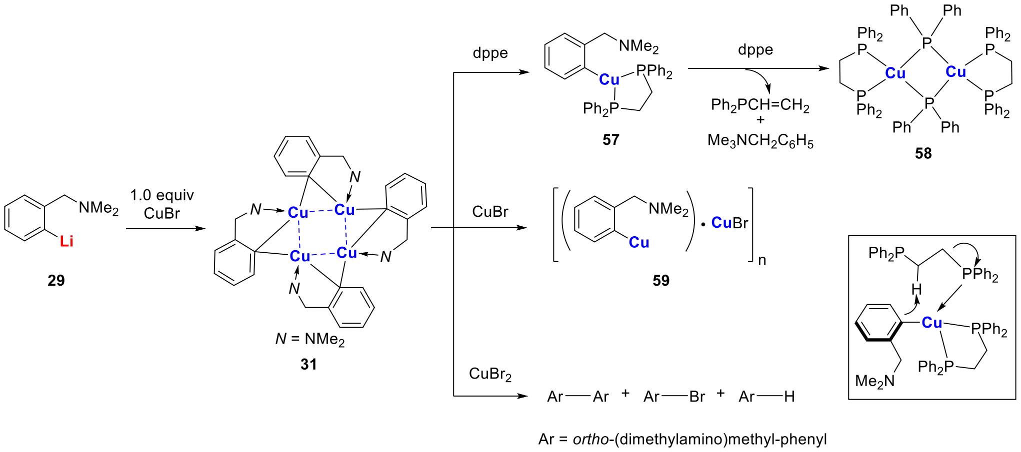
Scheme 13. Reactivity of bis-enyl organocopper aggregates

The reactivity of the above bis-enyl copper compounds was displayed by the reactions of **43** and **46** (Scheme 13). **43** afforded tricycle-octa-diene **47** and cyclopenta-2,4-dien-1-imine **48** via thermolysis and insertion of isocyanide, respectively. When heated in THF, **46** afforded multi-substituted cyclooctatetraene **49**. In toluene, thermolysis of **46** gave semibullvalene **50** as the major product, which was consistent with the early work[85].



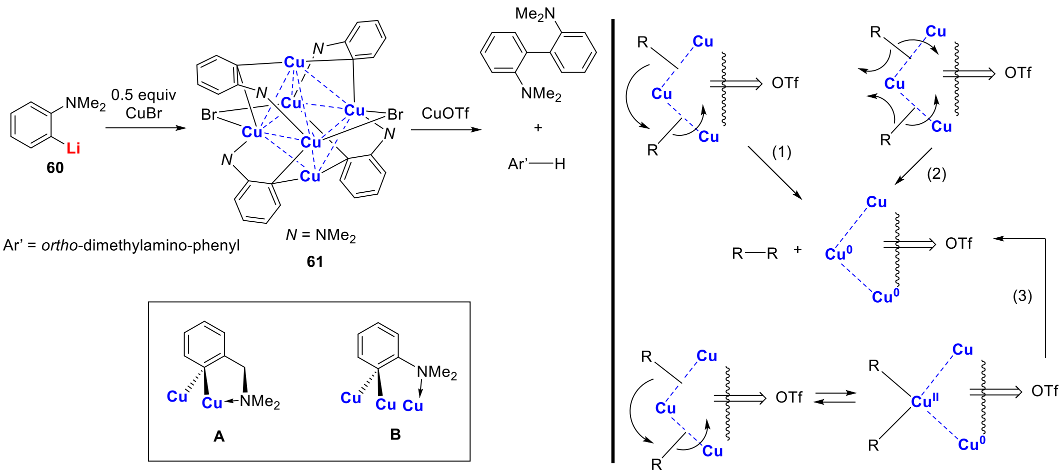
Scheme 14. Styrenyl and budadienyl organocopper aggregates

Copper-mediated reactions of zirconacyclopentadienes (or zirconaindenes) and electrophiles developed by Takahashi and others are extensively used to construct a variety of functional organic molecules[87,88]. However, the organocopper intermediates remain elusive, though the mythologies were reported about twenty years ago. Inspired by this work, Xi group revisited the transmetalation reaction of zirconium reagents and copper salts. Salt-free zirconaindenes **51** and zirconacyclopentadienes **52** were readily prepared according to the reported procedure[87]. 1:3 reaction of **51** and CuCl in THF/ TMEDA afforded a tetrameric styrenyl copper aggregate **53** in 53% isolated yield (Scheme 14). When **51** was treated with 2.5 equiv. of CuCl, a hexameric styrenyl copper aggregate **54** was obtained in 27% isolated yield after crystallization in Et_2O and tetrahydrothiophene (THT). Zirconacyclopentadienes **52a**,**b** reacted with 3.4 equiv. of CuCl in THF, affording trimeric butadienyl copper aggregate **55** and **56** in 72% and 51%, respectively. The additional ancillary ligand (TMEDA vs THT) could change the aggregate state of the styrenyl clusters. In the molecular structures, **53** consists of ten copper atoms, while **54** is a hexanuclear cluster with twelve copper atoms. The lengths of Cu-C(alkenyl) bonds (1.98-2.01 Å) are comparable to those of Cu-C(aryl) bonds (1.98-2.02 Å), as shown in **53**. The binding mode of **54** looks more complicated yet unique. **54** comprises two unusual μ_3-alkenyl carbon atoms (black dots: C17, C17′) and the corresponding two tri-coordinated copper atoms (red: Cu2, Cu2′). **55** and **56** share identical core copper structures. In addition, **55** and **56** can be regarded as variants of **44** by replacing two lateral lithium atoms with copper atoms. The substituents of butadienyl skeleton seem to have an influence on the stability of their copper clusters. In Et_2O, **55** is relatively stable below 10 ℃, whereas **56** is would thermally decompose and release the copper mirror at 10 ℃ within 0.5 h. The reactivity of **55** was provided by its coupling reaction with diiodobenzene, affording multi-substituted naphthalene.



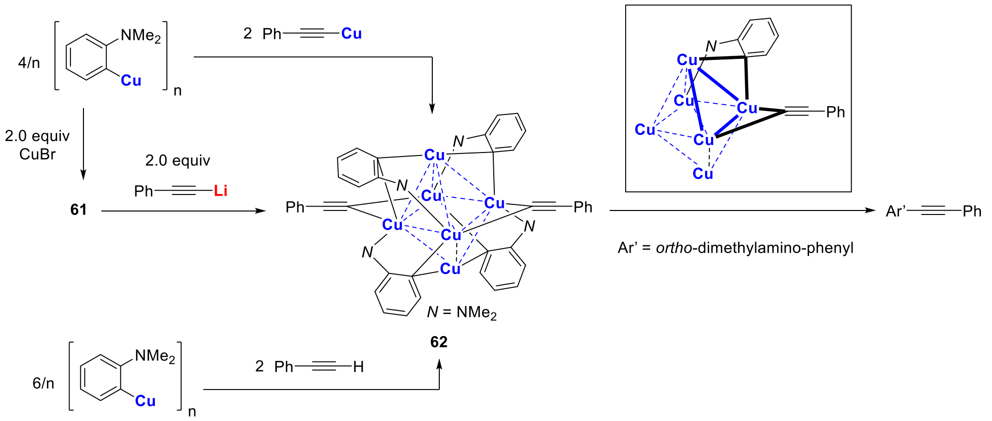
Scheme 15. Synthesis and reactivity of C,N-chelated tetranuclear organocopper cluster

Intramolecular stabilization effect developed by van Koten was initially used to synthesize organocopper clusters. The reaction of **29** with 1.0 equiv. of CuBr afforded a LiBr-free tetranuclear copper cluster **31**, which is thermally stable up to 170-185 ℃ (phenylcopper: slow decomposition at room temperature)[89,90]. The molecular structure of **31** comprises four copper atoms in a butterfly arrangement (Scheme 15)[91,92]. Each C_{ipso} bridges two copper atoms via 3c-2e Cu-C bonds (1.97-2.16 Å). Each copper atom has a distorted trigonal planar geometry. Variable temperature ^1H NMR spectroscopy shows that methylene and NMe_2 signals are singlets, independent on the temperatures, which suggest a weak $Me_2N \rightarrow Cu$ interaction in solution. Whereas the reaction between **31** and 1.0 equiv. of dppe afforded a 1:1 donor-acceptor copper complex **57**, the addition of excess dppe resulted in an unusual C-P bond cleavage, with the formation of a phosphidocopper complex **58**, $Ph_2PCH{=}CH_2$, and Ar-H[93,94]. The process could be explained by a concerted mechanism, as shown in the box. 1:1 reaction of **31** with CuBr affords a polymeric complex **59**. When cupric halides were used instead, oxidative coupling products Ar-Ar, Ar-X, and Ar-H were obtained[95]. In addition, van Koten and co-workers reported a serial of organocopper aggregates with the N-C-C-C-Cu connectivity supported on other C,N-bidentate ligands, such as 8-(dimethylamino)naphthyl[96], 2-oxazoline-4-methylphenyl[97,98], and (2-(dimethylamino)phenyl)-1-vinyl[99-102].



Scheme 16. C,N-chelated hexanuclear organocopper cluster and reactivities

When a built-in heteroatom moiety is directly attached to the phenyl skeleton, the C,N-bidentate ligand displayed different features when binding to the copper atoms (N-C-C-Cu connectivity). Van Koten reported that the treatment of **60** with copper bromide affords a hexanuclear copper cluster **61**, which includes six copper atoms in a distorted octahedral arrangement (Scheme 16)[103-106]. Each bromide atom bridges *trans*-equatorial edges. Each C,N-bidentate ligand bridges three copper atoms on a face of octahedron. Molecular weight determinations and ^{1}H NMR spectroscopy supported that **61** retained its aggregate structure in solution. Me_2N was observed as two broadened singlets (1.84, 2.92 ppm) at room temperature, suggesting a relatively strong $Me_2N \rightarrow Cu$ bonding interaction in contrast to that in **31**. When the temperature increases to 90 ℃, the two singlets coalesced to a singlet (2.42 ppm). In **31**, the C_{ipso} atom and Me_2N bind to the same copper atom, leading to a 5-membered chelate ring (**A**), whereas in **61**, $Me_2N \rightarrow Cu$ coordination takes place with a different copper atom to which the aryl group is not bonded (**B**), due to the steric effects. When **61** was treated with CuOTf, a selective, quantitative coupling of biaryls Ar′-Ar′ occurred as unexpected[107,108]. Only a trace amount of Ar′-H was formed, which excluded the pathway involving free radicals. The charge transfer from the core coppers to the strongly electron accepting OTf groups, which reduced the electron density of the core skeleton, accounts for the C-C bond formation. The proposed mechanism (3), including valence disproportionation inside the metal core followed by reductive elimination of Ar′-Ar′, rationalized the large influence of the identity of anions.



Scheme 17. Selective coupling from the thermolysis of hexanuclear organocopper cluster

Based on the early work shown in Scheme 16, van Koten reported that **62** could be synthesized via three methods (Scheme 17)[109-112]. Thermolysis of $Ar'_4(CCPh)_2Cu_6$ **62** results in an exclusive formation of the mixed coupling product Ar′-CCPh. The absence of Ar′-H or PhCC-H from hydrogen abstraction indicates that the reaction undergoes a concerted pathway rather than proceeds via free radicals. The molecular structure of **62** comprises exclusively triangular copper faces occupied by one Ar′ and one PhCC ligand, whereas $Cu_3Ar'_2$ or $Cu_3(CCPh)_2$ faces are absent, explaining the high selectivity of the asymmetric C-C bond formation.

6. Conclusion and Perspective

In this review, we have summarized structurally well-defined organocopper compounds based on C,N- and C,C-bidentate ligands, from mononuclear copper spiro compounds to polynuclear copper clusters. It was shown that the intramolecular stabilization effect of C,N-bidentate ligands and the cooperative effect of C,C-bidentate ligands (*cis*-1,3-butadienyl) could both enhance the solubility and stability of resulting organocopper compounds. In the molecular structures, copper(I) atoms adopt linear, trigonal, or tetrahedral geometries, depending on the coordination numbers. In charge-neutral copper aggregates, the electron-deficient 3c-2e Cu-C bonds are predominant, whereas in more electron-rich organocuprates, the Cu-C bonds have a much higher degree of 2c-2e bond character.

The strategy of enhancing the intramolecular coordination was further developed by adding two build-in heteroatom moieties to the aryl ring. Consequently, the original ligands turn into tridentate pincer ligands, e.g., C,N,N and N,C,N-ligands[29], which are now widely used in organic synthesis and small molecules activations. Another interest in organocopper chemistry was high-valent organocopper compounds[113]. It was found that the macrocyclic ligands with three intramolecular heteroatom moieties, e.g., C,N,N,N-cyclic ligands, were excellent platforms to support organocopper(III) compounds. Moreover, an increasing interest is growing in more challenging organocopper(II) compounds in recent years, since many Cu-catalyzed reactions may have Cu(II)-C containing species as the intermediates.

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