Organometallic Compounds

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Structure and Reaction Chemistry of Magnesium Organocuprates Derived from Magnesiacyclopentadienes and Copper(I) Salts

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Abstract: *The chemistry of magnesium organocuprates, including their synthesis, structures, and reactions, remains underexplored. In this work, by taking advantage of the high reactivity and ready availability of magnesiacyclopentadienes, a series of magnesiacyclopentadiene-based organocuprates were synthesized and structurally characterized. A variety of CuX salts (X = Cl, Br, I, or alkynyl) were successfully applied to react with magnesiacyclopentadienes. Besides CuX salts, AgX salts (X = Cl, alkynyl) also undergwent the above reaction to afford the corresponding magnesium organoargentates. Single-crystal X-ray structural analysis and DFT calculations of these butadienyl magnesium organocuprates revealed unique structural characteristics and bonding modes. These results are also very useful to understand the transmetalation process, since the product can be viewed as the resting-state intermediate of a transmetalation reaction between organomagnesium compounds and coinage-metal salts. Preliminary information on the reaction chemistry of these magnesium organocuprates is provided by their reactions with allyl bromide, benzoyl chloride, and* CO_2.

Organocopper(I) compounds are ubiquitously involved in Cu-based reactions as synthetic reagents or key intermediates.[1] Among these compounds, lithium organocuprates have been widely applied in synthetic chemistry. Many lithium organocuprates have been structurally characterized.[2] However, in sharp contrast, magnesium organocuprates remain almost unexplored, particularly in terms of their well-defined structures, although different structural characteristics and useful reaction chemistry can be expected. The limited examples of structurally characterized magnesium organocuprates are all based on aryl skeletons, for example, aryl magnesium organocuprates.[3] To the best of our knowledge, there have been no alkenyl magnesium organocuprates isolated to date.

We recently reported a facile synthesis of multisubstituted magnesiacyclopentadienes (**1**) as the first example of alkaline-earth metallocyclopentadienes.[4] Single-crystal X-ray structural analysis of these magnesiacyclopentadienes revealed a nearly coplanar ring skeleton. Although the lengths of the chemical bonds of the ring, including two Mg–C(sp^2) bonds, are comparable to those reported, the bite angle of C1-Mg-C4 (91.54°) is much smaller than the classic C-Mg-C angles in the usual tetracoordinate magnesium compounds (115–130°).[5] This structural information, including the nearly coplanar ring skeleton and the small bite angle, indicates that these magnesiacyclopentadienes should possess a high degree of ring strain and thus should be highly reactive. As part of our continued interest in butadienyl-based organometallic chemistry, we initiated research on the reaction chemistry of these magnesiacyclopentadienes with metal salts. We envisioned that the high reactivity of these magnesiacyclopentadienes would lead them to undergo facile transmetalation reactions with CuX to generate the corresponding magnesium organocuprates, in which the butadienyl skeleton should stabilize well-defined structures. Herein, we report the isolation and structural characterization of a series of novel monomeric (Cu/Mg = 1:2) and linearly linked dimeric (Cu/Mg = 2:3) magnesium organocuprates. These results also shed light on the transmetalation process,[6] since the product can be viewed as the resting-state intermediate of a transmetalation reaction between organomagnesium compounds and coinage-metal salts.

Treatment of magnesiacyclopentadiene **1a** with 0.5 equiv of copper(I) salt in hexane at room temperature for 1 h afforded a yellow precipitate. The solid was filtered and recrystallized in Et_2O and THF to give the magnesium organocuprates **2a**, **2b**, and **2c** in 71 %, 70 % and 79 % yields of isolated product, respectively (Scheme 1). When 0.75 and 1.0 equiv of copper(I) salts were reacted with **1a**, products **2** were always obtained as the major products. Similarly, when **1a** was reacted with 0.5 equiv of $AgCl{\cdot}PMe_3$, the corresponding magnesium organoargentate **2d** was isolated in 68 % yield. In addition, (phenylethynyl)copper(I) and (phenylethynyl)silver(I) were both compatible under similar reaction conditions (hexane/THF = 2:1), with more than 75 % conversions of **1a**, as determined by ^1H NMR spectroscopy in C_6D_6 with hexamethylbenzene as an internal standard. Finally, alkynyl magnesium organocuprate **3a** and alkynyl magnesium organoargentate **3b** were obtained in 41 % and 24 % yields of isolated product, respectively. When **1b** was treated with 0.5 equiv of copper(I) salt under the above-mentioned reaction conditions, different magnesium organocuprates (**4a** and **4b**) with a Cu/Mg ratio 2:3 were obtained as major products. After optimization of the reaction conditions

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Supporting information for this article (including experimental details, X-ray crystallographic data, and scanned NMR spectra of all new products) can be found under:
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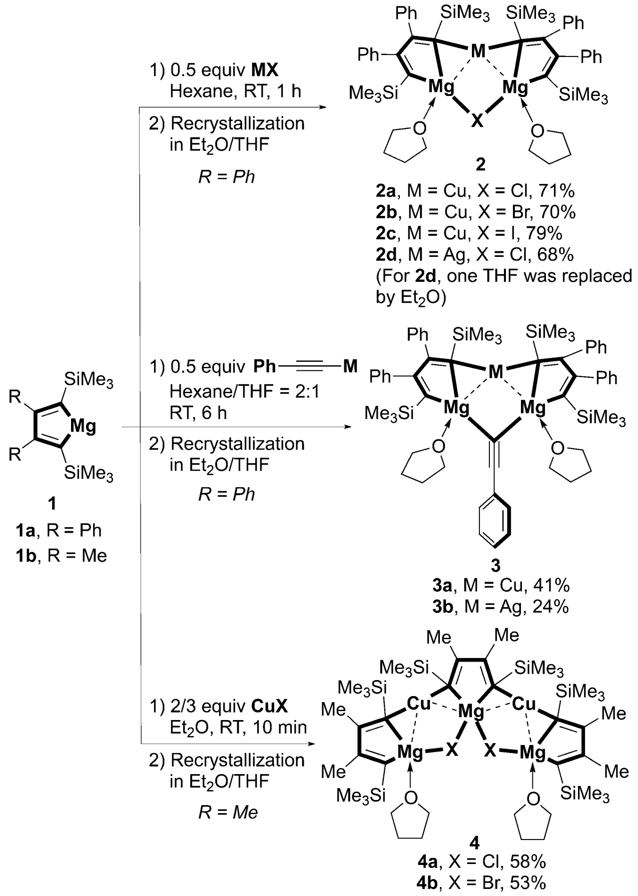


Scheme 1. Synthesis of magnesiacyclopentadiene-based magnesium organocuprates and organoargentates.

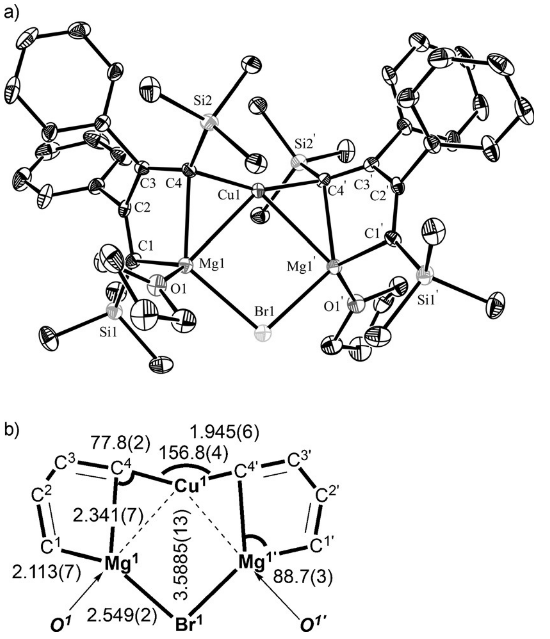


Figure 1. a) ORTEP drawing of **2b** with thermal ellipsoids drawn at 30% probability. H atoms are omitted for clarity. b) Selected bond lengths [Å] and bond angles (°) of **2b**.

(2/3 equiv CuX; Et_2O, RT, 10 min), magnesium organocuprates **4a** and **4b** were generated in 58% and 53% yields of isolated product, respectively. Products **2**–**4** were all obtained as air- and moisture-sensitive yellow crystals and subjected to single-crystal X-ray structural analysis. The results show that both inorganic and organic coinage-metal salts can be effectively fused with magnesiacyclopentadienes **1** through the formal cleavage of M−X bonds. Furthermore, the substituents of the butadienyl skeletons significantly influence the composition and configuration of the products.

Compounds **2a** and **2b** both crystallized in the orthorhombic *Fdd*2 space group, while **2c** crystallized in the monoclinic *P*21/*n* space group. Compounds **2a**, **2b**, and **2c** have almost identical configurations. Figure 1 shows the single-crystal X-ray structure of **2b** (for the structures of **2a** and **2c**, see the Supporting Information). Compound **2b** is symmetrical, with the line through Cu1 and Br1 as the *C*2 axis. Compound **2b** consists of two magnesiacyclopentadiene units linked by one discrete CuBr unit. The non-planar magnesiacyclopentadiene moieties in **2** are distorted, with C4, C4′ atoms bending away from the original five-membered plane toward the Cu atom. The Mg atoms are tetracoordinated by two alkenyl carbon atoms, one bromide atom, and one oxygen atom. Compared to that in the magnesiacyclopentadiene **1a**-TMEDA,[4] the Mg−C1 bond length [2.113(7) Å] almost does not change, while the Mg−C4 bond length [2.341(7) Å] increases noticeably in **2b**. Although the C1-Mg-C4 bite angle [88.7(3)°] became much smaller, the strained magnesiacyclopentadiene skeleton can be stabilized by Mg−Br bond formation [2.549(2) Å] and the resulting obtuse C-Mg-Br angles [(117.13(19)°, 128.92(19)°]. The Cu−C bond length [1.945(6) Å] is in the range of Cu−C(sp^2) bond lengths in diaryl organocuprates (1.91–2.35 Å).[2a] However, the C-Cu-C bond angle [156.8(4)°] is significantly less obtuse than that of diaryl lithium organocuprates (163–178°), which indicates that a higher degree of covalency in the Mg−C bond induces a corresponding increase in the Cu−C−Mg three-center-two-electron bonding character.[3f] The Cu−Mg distance [2.709(2) Å] is shorter than the sum of van der Waals radii of Cu (2.0 Å) and Mg (2.2 Å) atoms, which indicates a weak Cu−Mg interaction.[7] Overall, in analogy to lithium diorganocuprate–lithium halide aggregates,[8] the six central atoms (C4, C4′, Cu1, Mg1, Mg1′, and Br1) in **2b** form a monomeric magnesium organocuprate following an incomplete transmetalation event between magnesiacyclopentadienes and coinage-metal salts. In this process, the Br atom and one Mg−C bond are retained in the product skeleton, whereas they would be released as $MgBr_2$ salt in other general transmetalation reactions. Compound **2d** crystallized in the orthorhombic *Pbca* space group. The structure of **2d** is similar to that of **2b** except for a more distorted configuration and longer Ag−C bond lengths (for structural details of **2d**, see the Supporting Information). It is noteworthy that **2d** is the first example of a magnesium organoargentate.[9] Compounds **3a** and **3b** have analogous configurations to **2a** and **2d**, respectively, except for the bridging phenylethynyl ligands on two Mg atoms (for structures of **3a** and **3b**, see the Supporting Information).

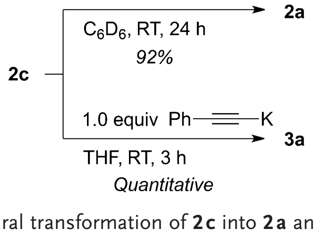
To gain further insight into the bonding situations of the magnesium organocuprates, DFT calculations were carried out by using natural bond orbital (NBO) analysis[10] and atoms in molecules (AIM) analysis.[11] Compound **2b** was structurally optimized at the B3LYP/LANL2DZ[12] (for Cu, Br) or 6-31 + G*[13] (for the other elements) level in the gas phase by Gaussian 09.[14] In the optimized structure, the configuration and all bond lengths were consistent with the X-ray structure. As shown in Table 1, NBO analysis of the Mg–C1 and Mg–C4 bonds clearly suggested one classical Mg–C(sp$^{2)}$ bond[5] and another drastically weakened Mg–C(sp^2) bond, respectively (Table 1, entry 1–2). The Wiberg bond index for Cu1–Mg1 indicates a weak Cu–Mg interaction, which is in accordance with the short distance in the single-crystal structure of **2b** (Table 1, entry 4). The Wiberg bond index of Cu1–Br1 was nearly zero, which indicates complete cleavage of the Cu–Br bond by two magnesiacyclopentadienes (Table 1, entry 6). AIM methods located a ring critical point (CP) in the six-membered ring (C4, Cu1, C4′, Mg1, Mg1′, Br1), while no bond path (or bond CP) was found between Cu and Br atoms, which supports the non-existence of a Cu–Br interaction (for details, see the Supporting Information). Furthermore, AIM analysis located no bond path (or BCP) between the Cu and Mg atoms, whereas the Mg–C bond paths are slightly bent toward the Cu atom. This result suggests that the Cu–Mg interaction is likely to be very weak.

Table 1: NBO calculations for **2b**.

Entry	Bond	Length [Å]	Wiberg Bond Index
1	Mg1–C1	2.1219	0.3823
2	Mg1–C4	2.3396	0.2150
3	Cu1–C4	1.9810	0.3375
4	Cu1–Mg1	2.7673	0.1543
5	Br1–Mg1	2.6232	0.3470
6	Br1–Cu1	3.7188	0.0482

As shown in Scheme 2, ^{7}Li and ^{1}H NMR spectroscopy demonstrate that when treated with an excess of LiCl in C_6D_6 at room temperature for 24 h, **2c** can be transformed into **2a** in 92% yield through a halide-exchange process. Moreover, **2c** reacted with 1.0 equiv of (phenylethynyl)potassium[15] in THF at room temperature over 3 h to afford **3a** quantitatively, as determined by ^{1}H NMR spectroscopy in C_6D_6.

Both **4a** and **4b** crystallized in the monoclinic *C*2/*c* space group. Compound **4a** is symmetrical, with the line through Mg2 and the center of C6-C6′ as the *C*2 axis (Figure 2). It comprises three nonplanar magnesiacyclopentadiene units and two separated CuCl units (for the structure of **4b**, see the Supporting Information). Compared to that in the corresponding magnesiacyclopentadiene **1b**-TMEDA,[4] the Mg–C5 bond is longer [2.2872(17) Å], while the Mg–C1 [2.0913(19) Å] and Mg–C4 [2.3086(18) Å] bonds become slightly shortened and dramatically elongated, respectively. The Cu–C bond lengths [1.9438(17), 1.9506(17) Å] and C-Cu-C bond angles [164.11(7)°] are both in the range expected for diaryl organocuprates.[2a] As the topological structure shows, dimeric **4a** can be regarded as a combination of two [(MeTMS-vinyl)$_2$Cu]$^-$ cuprate units and two [(MeTMS-vinyl) Mg$_{1.5}$Cl]$^+$ countercation units.



Scheme 2. Structural transformation of **2c** into **2a** and **3a**.

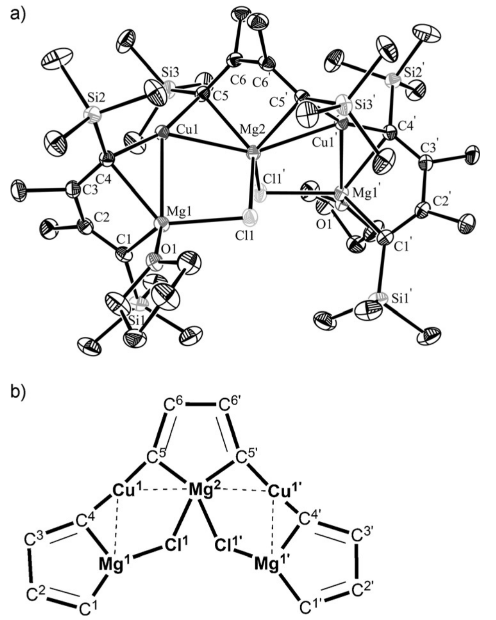
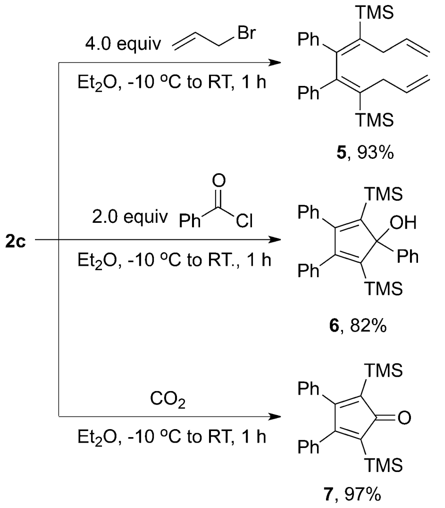


Figure 2. a) ORTEP drawing of **4a** with thermal ellipsoids drawn at 30% probability for non-H atoms. H atoms are omitted for clarity. b) Topological structure of **4a**. Me and SiMe$_3$ substitutes are omitted for clarity.

As an alternative perspective, magnesiacyclopentadienes in the above reactions act in the same way as amphiphilic ligands, with the more exposed terminal alkenyl carbon atoms as Lewis bases and the unsaturated magnesium atoms as Lewis acids.[16] The synergistic coordination of terminal C(sp^2) atoms and Mg atoms on MX salts leads to heterolytic cleavage of the M–X bonds through the transfer of anionic X units from M centers to Mg centers.[17] Accordingly, the magnesiacyclopentadienes could be considered as examples of ambiphilic ligands, with incorporation of Mg-based Lewis acids and C-based Lewis bases, which were previously limited to Group 13 (B, Al) and Group 15 (N, P) atoms.

The preliminary reactivity of magnesium organocuprate **2c**, which has four reactive sites (C1, C1′, C4, C4′), was investigated (Scheme 3). Treatment of **2c** with allyl bromide afforded bis-allylated product **5** in 93% yield of isolated product. Reaction of **2c** with benzoyl chloride (even with 3.0 equiv) gave the cyclization product **6**. 2,5-Bis(trimethylsilyl)-substituted cyclopentadienone **7** was obtained in 97% yield of isolated product from the reaction of **2c** with CO$_2$.

In summary, we have synthesized and structurally characterized a series of rigid alkenyl magnesium organocuprates



Scheme 3. Preliminary reactivities of **2c**.

or organoargentates based on s-*cis* 1,3-butadiene skeletons through synergistic activation of the Cu−X bonds by magnesiacyclopentadienes. The resulting magnesium ate complexes can be considered to be the resting-state intermediate of a transmetalation reaction between magnesiacyclopentadienes and copper(I)/silver(I) compounds. The novel finding is fundamentally significant for understanding the mechanism of transmetalation processes and the bonding characters of magnesium cuprates/argentates.

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Keywords: Cu−X bond cleavage · magnesiacyclopentadienes · magnesium organocuprates · organometallic compounds · transmetalation

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