

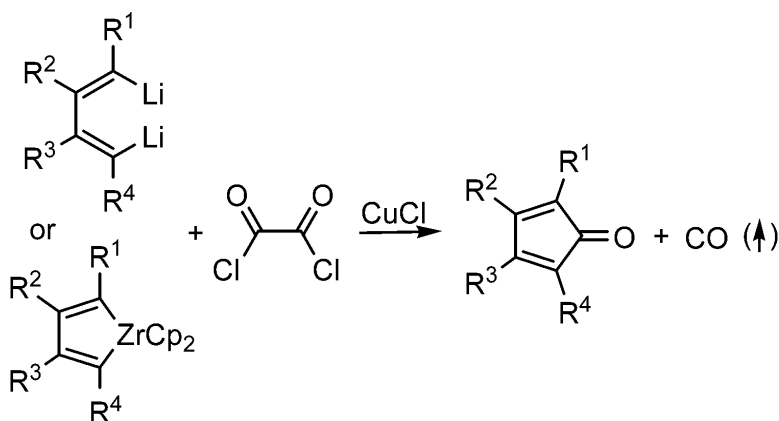
Communication

1,1-Cycloaddition of Oxalyl Dichloride with Dialkenylmetal Compounds: Formation of Cyclopentadienone Derivatives by the Reaction of 1,4-Dilithio-1,3-dienes or Zirconacyclopentadienes with Oxalyl Chloride in the Presence of CuCl

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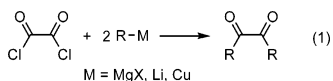
1,1-Cycloaddition of Oxalyl Dichloride with Dialkenylmetal Compounds: Formation of Cyclopentadienone Derivatives by the Reaction of 1,4-Dilithio-1,3-dienes or Zirconacyclopentadienes with Oxalyl Chloride in the Presence of CuCl

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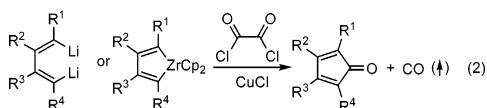
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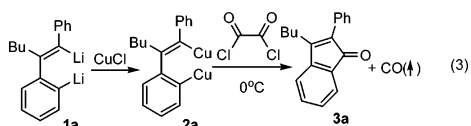
Oxalyl chloride, as carbonylated reagent, had been reported to undergo substitution reaction with 2 equiv of monofunctional organometallic compound, such as Grignard reagent, organolithium, and organocopper compound, to form 1,2-diorgano-1,2-dione (eq 1).¹



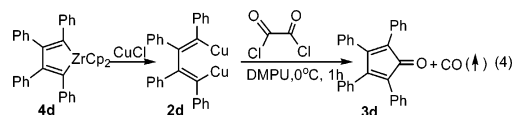
When dianionic reagents of these organometallic compounds were used, however, the reaction frequently led to the formation of complex, or inseparable, mixture owing to over-addition, polymerization, or decomposition. Therefore, cyclization reaction of organodimetallic reagent (such as organodilithium, organodicopper, or organodimagnesium reagent) with oxalyl chloride is rare, although a successful cyclization of 1,4-dilithio-1,3-dienes with dimethyl oxalates to afford *o*-benzoquinones has been reported.² To the best of our knowledge, no 1,1-cycloaddition of oxalyl chloride with dicarbanionic reagent has been reported in which oxalyl chloride acts as one carbonyl donor. Herein we report the first 1,1-cycloaddition of oxalyl chloride with 1,4-dilithio-1,3-dienes or zirconacyclopentadienes to afford cyclopentadienone derivatives in the presence of CuCl (eq 2), in which the carbon-carbon bond of 1,2-dicarbonyl cleaved during nucleophilic addition.³



The initial experiment showed that reaction of organodilithium **1a** with oxalyl chloride led to the formation of complex, inseparable mixture. Nevertheless, a trace amount of cyclopentadienone **3a** was detected by GC-MS. This result may be explained by the high reactivity of organodilithium and oxalyl chloride, which results in the desired reaction to be minor. To avoid the high reactivity of organodilithium compound, a proper tuning of the reactivity of organodimetallic reagents and oxalyl chloride is possible.⁴ Therefore, we conducted the reaction of organodilithium **1a** with oxalyl chloride in the presence of CuCl, in which organodilithium compound **1a** transformed into organodicopper compound **2a** that was a softer nucleophile. The reaction smoothly proceeded, and cyclopentadienone⁶ was obtained in high yield with CO gas generated (eq 3).

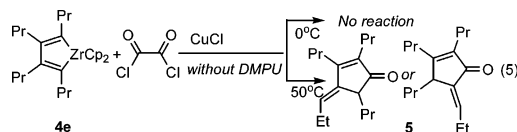


To extend the reaction of 1,4-dicopper-1,3-diene derivatives **2**, we tried various 1,4-dicopper-1,3-dienes that easily generated in situ from the corresponding zirconacyclopentadienes **4** and CuCl.⁷ For example, the reaction of 1,4-dicopper-1,3-diene **2d** with oxalyl chloride in the presence of 2 equiv of DMPU (*N,N'*-dimethylpropyleneurea)⁸ at 0 °C for 1 h led to compound **3d**⁹ in excellent yield (eq 4). Meanwhile, generated gas was collected and detected by GC. Only CO gas was measured, and no carbon dioxide was detected.



Listed in Table 1 are representative examples of cyclopentadienone derivatives **3** obtained by the reaction with zirconacyclopentadienes or 1,4-dilithio-1,3-dienes. Both could be symmetrically and unsymmetrically substituted dienes bearing alkyl and aryl groups.

It was noteworthy that 1,4-dicopper-1,3-dienes, which generated from the corresponding zirconacyclopentadienes **4**, did not react with oxalyl chloride at 0 °C in the absence of DMPU. This is in contrast to the reaction with 1,4-dicopper-1,3-dienes, which generated from the corresponding 1,4-dilithio-1,3-dienes **1**. When the reaction temperature was raised to 50 °C, the double bond rearranged product **5** was obtained in 69% isolated yield (eq 5). We propose that **5** formed via **3e**. To obtain the direct evidence, we treated **3e** in THF in the presence of CuCl at 50 °C, and **5** was obtained. These results indicated that in this reaction the DMPU was necessary not only for increasing the solubility of 1,4-dicopper-1,3-dienes in THF⁸ but also for activating the C-Cu bond to afford cyclopentadienone at low temperature.



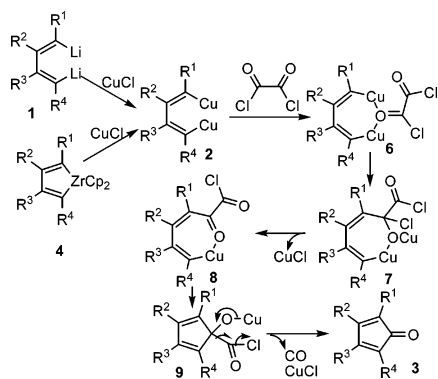
In light of these results, we propose a possible mechanism for this reaction (eq 6). First, the dialkenyl lithium compound **1** or the zirconacyclopentadiene **4** undergoes transmetalation with CuCl to form the dialkenylcopper compound.^{2,5,8,10} Second, coordination of one of the two carbonyl groups to copper metals of the alkenylcopper moieties affords seven-membered ring **6**. One of the two alkenylcopper moieties reacts with the chelated carbonyl group to form **7**. Then elimination of CuCl recovers coordinated C=O bond to form **8**, which then undergoes an intramolecular attack by the remaining alkenylcopper moiety to give five-membered carbocycle

Table 1. Reaction of Dianionic Reagents with Oxalyl Chloride

Entry	dianionic reagents	Cyclopentadienone	Yield(%) ^a
1			-(68) ^b
2			75 (63)
3			79 (65)
4			-(67) ^c
5			96 (87)
6			94 (82)
7			-(50)
8			71 (50)
9			-(49)

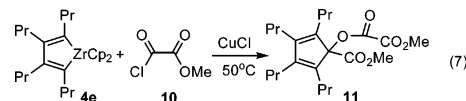
^a GC yields and isolated yields are given in parentheses. ^b 16.3 mL of CO gas was observed. ^c 16.5 mL of CO was observed. The yield of CO gas was comparable with the yield of cyclopentadienone.

9. Finally, elimination of the other CuCl accompanying decarbonylation gives product **3**. This result is in sharp contrast to the case of other dianionic reagent reactions with oxalyl chloride, which usually gives complex and inseparable products. The chelating effect of the alkenylcopper moieties and the formation of cyclopentadienone derivatives and CO gas were assumed to be the driving force in this reaction.



To further confirm the reaction mechanism, we carried out the reaction of 1-copper-1,4-diene, which generated in situ from the corresponding 1-lithium-1,4-diene and CuCl, with oxalyl chloride at 0 °C, in which there is no possibility to form a chelated intermediate. The starting material was completely consumed, however, and no 1,2-dione derivative was obtained. Instead, a complex mixture was obtained. This result indicates that the chelated

intermediate **6** is the most likely intermediate. This can prevent intermolecular reactions that give a complex mixture. Moreover, when the reaction was treated with dimethyl oxalate under the same reaction conditions, it did not proceed, and starting material remained. When the reaction was treated with methyl(chloro-carbonyl)formate **10** under the same reaction conditions, product **11** was obtained in 46% isolated yield after normal workup (eq 7). In this case, elimination of CuOMe and CO did not occur, whereas further reaction with the second molecule of **10** occurred. These results suggest that the intermediate **9** with chlorine is the most possible intermediate to afford cyclopentadienone.



In summary, 1,4-dithio-1,3-dienes or zirconocyclopentadienes unprecedentedly reacted with oxalyl chloride in the presence of CuCl, resulting in the formation of cyclopentadienones as 1,1-cycloaddition products. The investigation for the mechanism and scope are being undertaken in this laboratory.

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Supporting Information Available: Experimental procedure and spectroscopic data for new products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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