

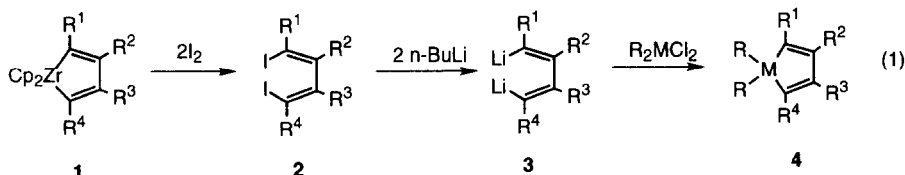
Remarkable Effect of Copper Chloride on Diiodination of Zirconacyclopentadienes

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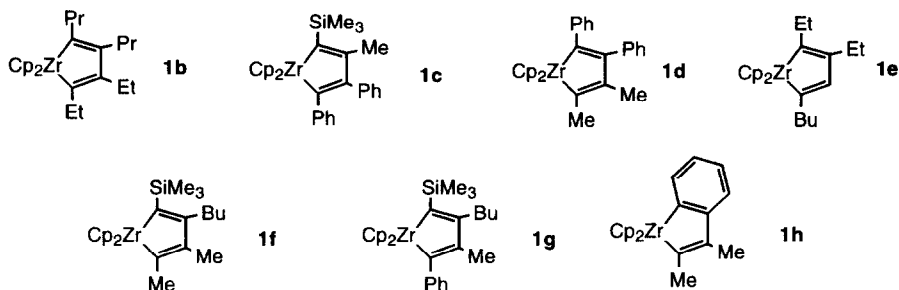
Abstract: Treatment of zirconacyclopentadienes with two equiv of iodine in THF in the presence of 1.0 equiv of CuCl gave diiododienes in good to high yields without formation of monoiododienes. This is in sharp contrast to the case without CuCl which afforded monoiododienes as major products. For zirconacyclopentenes, CuCl was also effective but the use of ICl was more practical. When zirconacyclopentenes were treated with 2 equiv of ICl, only diiodination products were formed. Preparation of silacyclopentadienes or spiro compounds using the diiododienes was demonstrated.
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Zirconacyclopentadienes which can be easily prepared from two alkynes are useful intermediates for organic syntheses.^{2,3} Various metallacyclopentadienes containing main elements such as Ge and Sn have been prepared by a direct reaction of zirconacyclopentadienes with metal halides such as GeCl₄ and SnCl₄.³ However, it is known that the direct reaction of the zirconacyclopentadienes with SiCl₄ or R₂SiCl₂ does not give the desired silacyclopentadiene derivatives.



In order to synthesize the silacyclopentadienes from the zirconacyclopentadienes, diiododienes **2** are necessary to be prepared by the iodination of zirconacyclopentadienes and then the reaction of their dilithiated dienes **3** with silylhalides provides the desired silacyclopentadienes according to the literature.⁴⁻⁶ However, one intrinsic problem of this method is the diiodination of the zirconacyclopentadienes. In most cases, the reaction of zirconacyclopentadienes with 2 equiv of iodine in THF produces a relatively large amount of monoiodination compounds. In the case of **1a**, monoiodination compound **5a** was the major product of the reaction as shown in eq (2). Employment of a longer reaction time or a higher temperature (50°C) does not improve the situation. When a large excess amount of iodine (4 equiv) was used, the yield of the diiodide was improved to around 70%. Monoiodides were still formed in 10 to 20 % yields. An alternative procedure was to change the solvent from THF to CH₂Cl₂.⁷ However, changing the solvent is usually inconvenient, especially in a large-scale reaction. In this paper we would like to report the remarkable effect of CuCl on the diiodination reaction of zirconacyclopentadienes.

To zirconacyclopentadiene **1a** which was prepared *in situ* from 2 mmol of 3-hexyne, Cp₂ZrCl₂ (1 mmol) and n-BuLi (2 mmol) in THF (5 mL) according to the literature⁸ were added 1 mmol of CuCl and 2 mmol of



A similar effect of CuCl was also expected for diiodination of zirconacyclopentenes.¹⁰ However, one of the two carbons attached to zirconium is a sp^3 carbon in zirconacyclopentenes.¹¹ Therefore, the effect of CuCl was slightly different from the case of the zirconacyclopentadienes. With one equiv of CuCl, diiodides were selectively or predominantly formed but prolonged reaction time (24h) was required. Unfortunately, a small amount of monoiodide¹² still remained. In order to prepare diiodides from the zirconacyclopentenes, commercially available ICl was more effective and practical. At room temperature after 1h, only the desired diiodides were formed in 79 and 86% yields for **6b** and **6c**, respectively (Table 2).

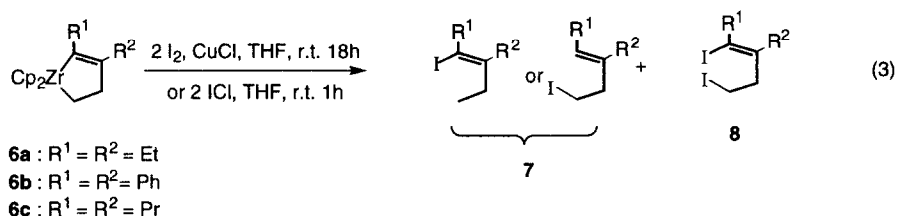
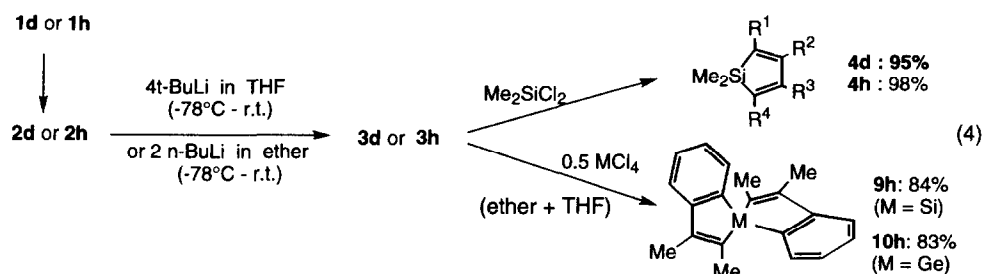


Table 2. Diiodination of zirconacyclopentenes.^a

Zirconacyclopentenes	Iodination reagent	Time/h	7	8
6a	CuCl (1 eq) + I ₂ (2 eq)	24	6	83 (63)
6b	CuCl (1 eq) + I ₂ (2 eq)	24	0	90 (69)
6b	ICl (2 eq) ^b	3	0	86 (71)
6c	ICl (2 eq) ^b	3	0	79 (59)

^a Solvent: THF, Temperature: room temperature. ^b ICl in THF was used. ICl in THF was prepared by addition of ICl to THF at 0°C.

As a demonstration, diiododienes prepared from the unsymmetrical zirconacyclopentadienes were used to prepare the silacyclopentadienes or spiro compounds. The lithiation procedure was dependent on the diiodides. For example, a reaction of **2d** with 4 equiv of *t*-BuLi in THF to afford dilithiated product **3d** proceeded cleanly, whereas **2h** gave dilithiated product **3h** when it was treated with 2 equiv of *n*-BuLi in ether. Reaction of these dilithiated compounds **3d** and **3h** with Me₂SiCl₂ gave **4d** and **4h** in 95% and 98% yields, respectively. Use of 2 equiv of **3h** for 1 equiv of SiCl₄ and GeCl₄ produced spiro products **9h** and **10h** in 84% and 83% yields, respectively.¹³



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- 9h**: $^1\text{H NMR}$ (CDCl_3) δ 1.83 (s, 6H), 2.21 (s, 6H), 7.16 (dt, $J=7.0, 1.3$ Hz, 2H), 7.26-7.45 (m, 6H). $^{13}\text{C NMR}$ (CDCl_3) δ 13.02, 13.73, 120.69, 126.21, 130.40, 130.76, 130.78, 132.51, 151.94, 153.47.
10h: $^1\text{H NMR}$ (CDCl_3) δ 1.93 (s, 6H), 2.16 (s, 6H), 7.14 (dt, $J=6.7, 2.1$ Hz, 2H), 7.32-7.39 (m, 6H). $^{13}\text{C NMR}$ (CDCl_3) δ 12.96, 15.66, 121.67, 126.42, 129.63, 132.44, 133.34, 133.44, 146.70, 151.09.

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