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## 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 diidodienes was demonstrated. © 1997 Elsevier Science Ltd.

Zirconacyclopentadienes which can be easily prepared from two alkynes are useful intermediates for organic syntheses.<sup>2,3</sup> Various metallacyclopentadienes containing main elements such as Ge and Sn have been prepared by a direct reaction of zirconacyclopentadienes with metal halides such as GeCl<sub>4</sub> and SnCl<sub>4</sub>.<sup>3</sup> However, it is known that the direct reaction of the zirconacyclopentadienes with SiCl<sub>4</sub> or R<sub>2</sub>SiCl<sub>2</sub> 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.<sup>4-6</sup> 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  $CH_2Cl_2$ .<sup>7</sup> 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, Cp<sub>2</sub>ZrCl<sub>2</sub> (1 mmol) and n-BuLi (2 mmol) in THF (5 mL) according to the literature<sup>8</sup> were added 1 mmol of CuCl and 2 mmol of

iodine at 0°C and the mixture was warmed to room temperature. After stirring the mixture at room temperature for 1h, diiodide **2a** was obtained in 95% yield. Formation of monoiodide **5a** was not observed.

Recently we have reported the facile transmetalation of the organic moiety of the zirconacyclopentadienes from zirconium to copper.<sup>2b-d</sup> Therefore, we first added two equiv of CuCl to **1a**. With 2 equiv of CuCl, the yield of diiodide **2a** was not better than 70%. This is because the corresponding dienyldicopper compound was not stable enough under the conditions used here. When one equiv of CuCl was used, a satisfactory result (**2a**: 95% yield; **5a**: 0%) was obtained. Since the iodination of the first carbon-zirconium in **1a** is relatively fast, addition of CuCl is effective for the iodination of the second carbon-zirconium bond. Transmetalation of the second carbon from zirconium to copper is a key step of this reaction. Reaction of the resulting **4**iododienylcopper compound with iodine gives the desired diiododiene **2a**. Use of other copper compounds such as CuBr, CuI, and CuCN afforded some amount of **5a** as shown in Table 1. A catalytic amount of CuCl (0.5 eq) did not show any remarkable effect on diiodination.

$$Cp_{2}Z_{f} \xrightarrow{Et} Et \xrightarrow{2l_{2}, CuCl, THF}_{Ft} \xrightarrow{I} \xrightarrow{Et}_{Et} Et \xrightarrow{t} I \xrightarrow{Et}_{Et} Et$$

$$Ia \xrightarrow{t} 1a \xrightarrow{t} 1a$$

Recently we have reported a convenient preparative method of unsymmetrical zirconacyclopentadienes 1 from two different alkynes.<sup>9a</sup> Diiodination of these unsymmetrical zirconacyclopentadienes 1b-h in the presence of one equiv of CuCl gave diiodides 2 in good to excellent yields. In all cases monoiodides 5 were not formed as shown in Table 1.

Zirconacyclopentadienes <sup>a</sup>	CuX (n eq)	Solvent	I <sub>2</sub> (n eq)	Temp. /°C	Time /h	Monoiodide 5 (%)	Diiodide 2 (%)
1a	_	THF	2	r.t.	6	70	18
1a	-	THF	2	50	1	78	22
1a	-	THF	4	r.t.	1	26	80
1a	_	$CH_2Cl_2$	2	r.t.	1	18	73
1a	CuCl (2.0)	THF	2	r.t.	1	0	70
1a	CuCl (1.0)	THF	2	r.t.	1	0	95
1a	CuBr (1.0)	THF	2	r.t.	1	2	82
1a	CuI (1.0)	THF	2	r.t.	1	10	79
1a	CuCN (1.0)	THF	2	r.t.	1	20	53
1 b	CuCl (1.0)	THF	2	r.t.	1	0	79
1 c	CuCl (1.0)	THF	2	r.t.	1	0	66
1 d	CuCl (1.0)	THF	2	<b>r</b> .t.	1	0	94
1 e	CuCl (1.0)	THF	2	r.t.	1	0	92
1f	CuCl (2.0)	THF	2.1	r.t.	1	0	73
1 g	CuCl (2.0)	THF	2.1	r.t.	1	0	57
1h <sup>b</sup>	CuCl (1.0)	THF	2	r.t.	1	0	76

Table 1. Reaction conditions of diiodination of zirconacyclopentadienes 1.

<sup>a</sup>Zirconacyclopentadiene **1a-1h** were *in situ* prepared in THF.<sup>8,9a</sup> <sup>b</sup>When **1h** was prepared in benzene, the diiodide was cleanly formed without CuCl.



A similar effect of CuCl was also expected for diiodination of zirconacyclopentenes.<sup>10</sup> However, one of the two carbons attached to zirconium is a  $sp^3$  carbon in zirconacyclopentenes.<sup>11</sup> 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 monoiodide<sup>12</sup> 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 zirconacyclopentene	es.a
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Zirconacyclopentenes	lopentenes Iodination reagent		7	8
ба	CuCl (1 eq) + $I_2$ (2 eq)	24	6	83 (63)
6 b	$CuCl (1 eq) + I_2 (2 eq)$	24	0	90 (69)
6 b	ICl (2 eq) <sup>b</sup>	3	0	86 (71)
6c	ICl (2 eq) <sup>b</sup>	3	0	79 (59)

 $^{\rm a}$  Solvent:THF, Temperature: room temperature.  $^{\rm b}$  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 Me<sub>2</sub>SiCl<sub>2</sub> gave 4d and 4h in 95% and 98% yields, respectively. Use of 2 equiv of 3h for 1 equiv of SiCl<sub>4</sub> and GeCl<sub>4</sub> produced spiro products 9h and 10h in 84% and 83% yields, respectively.<sup>13</sup>



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- 13. **9h**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.83 (s, 6H), 2.21 (s, 6H), 7.16 (dt, J=7.0, 1.3 Hz, 2H), 7.26-7.45 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.02, 13.73, 120.69, 126.21, 130.40, 130.76, 130.78, 132.51, 151.94, 153.47. **10h**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.93 (s, 6H), 2.16 (s, 6H), 7.14 (dt, J=6.7, 2.1 Hz, 2H), 7.32-7.39 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  12.96, 15.66, 121.67, 126.42, 129.63, 132.44, 133.34, 133.44, 146.70, 151.09.

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