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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 .O equiv ofCuCl gave diiododienes in good to high yields without formation of monoiododienes. This is in sharp contrast to the case wtthout CuCl which afforded monoiododienes as major products. For rirconacyclopentenes. CuCl was also effective but the use of ICI was more practical. When**  zirconacyclopentenes were treated with 2 equiv of ICI, only diiodination products were formed. **Preparation of silacyclopentadienes or Spiro compounds using the diidodienes was demonstrated. 0 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  $SiCl_4$  or  $R_2SiCl_2$  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 **la,** monoiodination compound **Sa** 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 **la** which was prepared in siru from 2 mm01 of 3-hexyne, Cp2ZrClz (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 1 h, diiodide **2a** was obtained in 95% yield. Formation of monoiodide **Sa** 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 **la**. 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; Sa: 0%) was obtained. Since the iodination of the first carbon-zirconium in **la** 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, Cul, 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.



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 I.

Zirconacyclopentadienes <sup>a</sup>	CuX $(n \t eq)$	Solvent	I <sub>2</sub> $(n \text{ eq})$	Temp. Æ	Time h	Monoiodide 5(%)	Diiodide 2(%)
1a		<b>THF</b>	$\overline{2}$	r.t.	6	70	18
1a		<b>THF</b>	$\overline{2}$	50	1	78	22
1a		<b>THF</b>	$\overline{4}$	r.t.	ł	26	80
1a		CH <sub>2</sub> Cl <sub>2</sub>	2	r.t.	I	18	73
1a	CuCl $(2.0)$	<b>THF</b>	$\overline{2}$	r.t.	1	$\mathbf 0$	70
1a	CuCl $(1.0)$	<b>THF</b>	$\overline{2}$	r.t.	1	$\mathbf 0$	95
1a	CuBr(1.0)	THF	$\overline{2}$	r.t.		$\overline{2}$	82
1a	$CuI$ (1.0)	<b>THF</b>	2	r.t.		10	79
1a	$CuCN$ $(1.0)$	<b>THF</b>	$\overline{2}$	r.t.	$\mathbf{1}$	20	53
1 <sub>b</sub>	CuCl (1.0)	<b>THF</b>	$\overline{c}$	r.t.	1	$\mathbf 0$	79
1 с	CuCl (1.0)	<b>THF</b>	$\overline{2}$	r.t.	1	$\mathbf 0$	66
1 <sub>d</sub>	$CuCl$ $(1.0)$	THF	$\mathfrak{2}$	r.t.		0	94
1e	CuCl(1.0)	THF	$\overline{c}$	r.t.		$\Omega$	92
1f	CuCl $(2.0)$	<b>THF</b>	2.1	r.t.		$\Omega$	73
1g	$CuCl$ (2.0)	<b>THF</b>	2.1	r.t.		0	57
1h <sub>b</sub>	CuCl(1.0)	<b>THF</b>	2	r.t.		0	76

Table 1. Reaction conditions of diiodination of zirconacyclopentadienes **1.** 

<sup>3</sup>Zirconacyclopentadiene **1a-1h** were *in situ* prepared in THF.<sup>8,9a</sup> bWhen **1h** was prepared in benzene, the diiodide was **cleanly formed wthout CuCI.** 



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  $sp<sup>3</sup>$  carbon in zirconacyclopentenes.<sup>11</sup> Therefore, the effect of CuCl was slightly different from the case of the zirconacyclopentadienes. With one equiv of CuCI, 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 lh, only the desired diiodides were formed in 79 and 86% yields for **6b** and 6c, respectively (Table 2).







**a Solvenr:THF, Temperature: room temperature. b ICI in THF was used. ICI in THF was prepared by addition of ICI 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 Sic14 and GeC14 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). '3C NMR (CDCIj) 6 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 (CDC13)  $\delta$  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>) 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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