

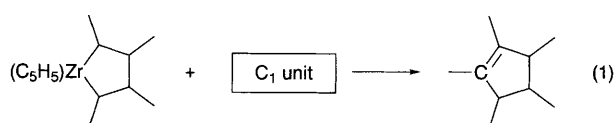
Formation of a Five-membered Carbocyclic Ring by Reaction of Zirconacyclopentane with RCOCl (R = Ph, Prⁱ, Et)

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Zirconacyclopentane reacts with RCOCl in the presence of a catalytic amount of CuCl/LiCl to give a five-membered carbocyclic ring.

Zirconacyclopentane is a very attractive compound since it is easily prepared from alkenes or dienes.^{1–4} In order to produce a five-membered carbocyclic ring from a zirconacyclopentane, a one carbon unit is required. Only carbon monoxide^{2,4} or isonitrile³ have been used so far as the one carbon unit with zirconacycles such as zirconacyclopentanes. In this paper we report that zirconacyclopentanes react with RCOCl (R = Ph, Prⁱ, Et) in the presence of a catalytic amount of CuCl/LiCl to give five-membered carbocyclic ring compounds, eqn. (1).



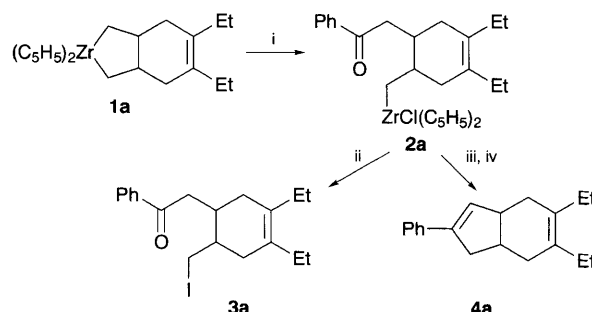
To a solution of zirconacyclopentane **1a**,^{1d} which was prepared from 4,5-diethylocta-1,4,7-triene and Negishi's reagent [(C₅H₅)₂ZrCl₂, BuⁿLi (2 equiv.)], was added a catalytic amount of CuCl (10 mg, 0.1 mmol) and benzoyl chloride (141 mg, 1.0 mmol) at –10 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. Cyclopentene derivative **4a** was obtained in 75% yield after treatment with 3 mol dm^{–3} HCl (Scheme 1).

Cyclopentene derivatives **4a–e** were obtained from **1a–c** in good to high yields (Table 1). In order to investigate the reaction mechanism, the reaction was quenched with iodine before warming to room temperature, yielding products **3a–e** as shown in Table 1. This suggests that the intermediate has an alkyl–zirconium bond and a ketone group. The reaction of **1b** was monitored by NMR spectroscopy and formation of **2b** was observed. Its ¹H NMR spectrum showed two singlets at δ 6.14 and 6.17 assigned to the (C₅H₅) rings. The ¹³C NMR spectrum showed two cyclopentadienyl signals at δ 112.89 and 113.14, and indicated that **2b** has a carbonyl group (δ 200.16), and methylene carbons attached to zirconium (δ 56.43). Iodination of **2b** gave **3b** as described above. This clearly indicated that the

copper catalysed carbon–carbon bond formation with RCOCl in the first step at –10 °C gives **2**.

Copper catalysed or mediated carbon–carbon bond formation reaction of zirconacyclopentadienes or zirconacyclopentenes has been recently reported by our group.^{4–6} A plausible mechanism of the first step of zirconacyclopentanes with PhCOCl involves a transmetalation of an alkyl carbon attached to zirconium to copper giving **5** as observed for other systems.^{4–6} It is known that alkylzirconocene chlorides such as (C₅H₅)₂ZrR¹Cl react with R²COCl to give acylation products R¹COR² in the presence of a copper catalyst.⁷

It is very interesting that only one alkyl carbon attached to zirconium reacts with RCOCl at –10 °C, although there are two alkyl–zirconium bonds in zirconacyclopentanes **1a–c**. Double acylation products were not obtained at –10 °C. When Bu^tCOCl was used with **1c**, the sequential cyclization did not proceed due to steric factors. The first alkyl–zirconium bond reacted with Bu^tCOCl at –10 °C to give **6** in 83% yield after hydrolysis of **7**. Even in the presence of an excess of Bu^tCOCl, only one alkyl–zirconium bond reacted. However, warming of

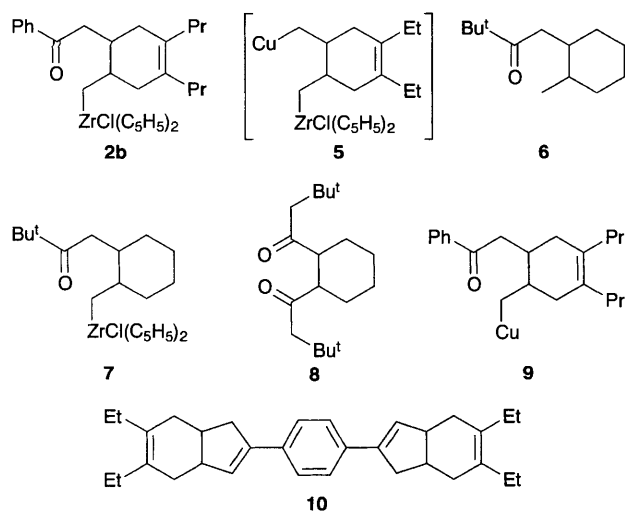


Scheme 1 Reagents and conditions: i, PhCOCl, cat. CuCl/LiCl; ii, I₂; iii, 24 h, room temp.; iv, H⁺

Table 1 Reaction of zirconacyclopentane with RCOCl in the presence of a catalytic amount of CuCl

Zirconacyclopentane	RCOCl	Iodination Product		Cyclised Product	
		3	Yield (%) ^a	4	Yield (%) ^a
	PhCOCl	3a	95 (63)	4a	75 (54)
	PhCOCl	3b	75 (60)	4b	58 (50)
	PhCOCl	3c	64 (53) ^d	4c	95 (84) ^{d,e}
	Pr ⁱ COCl	3d	64 (56) ^d	4d	76 (55) ^{d,e}
	EtCOCl	3e	55 (48) ^d	4e	68 (56) ^{d,e}

^a GC yields. ^b Only *cis* isomer, ref. 1d. ^c A mixture of *cis* and *trans* (5:1), ref. 2b. Isolated yields are given in parentheses. ^d A mixture of *cis* and *trans*. ^e Contains double bond positional isomers.



the mixture to room temperature afforded the corresponding double acylation product **8** in 89% yield. The different reactivity of two alkyl-zirconium bonds of zirconacyclopentanes is due to the strain in the zirconacyclopentane system.⁸ This is in sharp contrast to the case of dialkylzirconocenes such as $(C_5H_5)_2ZrMe_2$ where both methyl groups showed a similar reactivity toward $PhCOCl$ in the presence of a catalytic amount of $CuCl$.

Intermediate **2b** intramolecularly cyclized to give **4b** when the reaction mixture was stirred for 24 h at room temperature and treated with 3 mol dm^{-3} HCl . This type of intramolecular nucleophilic attack of zirconium compounds to carbonyl group

is unprecedented even after transmetalation from zirconium to copper. It is not clear yet but both of **2b** and **9** should be considered as the species which cyclized. Application of this reaction to a bridged cyclopentene compound was achieved, when terephthaloyl chloride was used, yielding symmetrical **10** (48%).

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