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Preparation of 1,2,3-Trisubstituted Cyclopentadienes and Tetrahydroindene Derivatives from Zirconacyclopentenes

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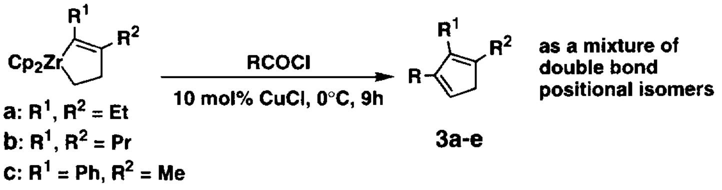
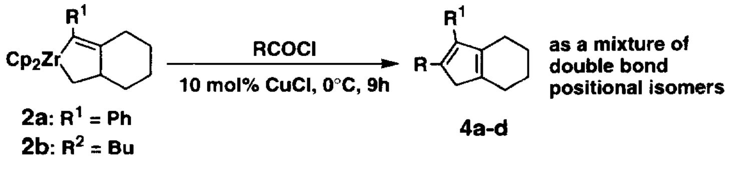
Abstract: 1,2,3-Trisubstituted cyclopentadienes and tetrahydroindene derivatives were prepared by a one-step reaction from zirconacyclopentene complexes, which are easily prepared from alkynes and EtMgBr (or ethylene) and Cp_2ZrCl_2. Reaction of zirconacyclopentenes with phthaloyl chlorides afforded intramolecular Michael addition reaction products. The structure of one of the products was determined by X-ray study. Copyright © 1996 Elsevier Science Ltd

The carbon-carbon bond formation reaction of zirconacyclopentenes is very attractive since zirconaccyclopentenes can be easily prepared by the reaction of an alkyne with zirconocene ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ or zirconacyclopentane.[1] We have studied the one-step ring closure of zirconacyclopentenes to provide cyclopentadiene derivatives. Cyclopentadiene derivatives have been widely used for organometallic complexes as ligands.[2] In particular, metallocene complexes with various cyclopentadienyl ligands have been intensively investigated in relevance to the polyolefin industry.[3] Recently, Chung and coworkers[4] have reported the first general preparative method of 1,2,3-trisubstituted cyclopentadienes which involves a Pauson-Khand reaction and a retro-Diels-Alder reaction. In this paper we would like to report a one-step preparation of 1,2,3-trisubstituted cyclopentadienes and tetrahydroindene derivatives from zirconacyclopentenes. We also report that the reaction of zirconacyclopentenes with phthaloyl chloride afforded intramolecular Michael addition products as stable compounds.



(1)



(2)

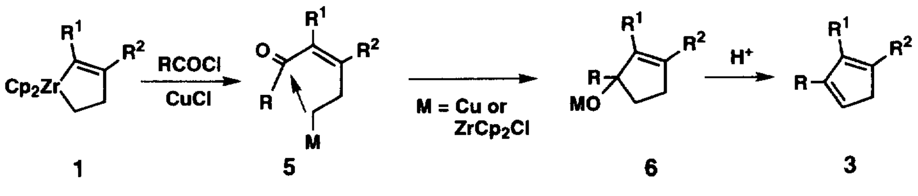
Reactions were carried out as follows. To a mixture of zirconacyclopentene **1a** (1 mmol), which was prepared by using 3-hexyne and Cp_2ZrEt_2 (or Cp_2ZrBu_2/ethylene),[4] was added benzoyl chloride (1.0 mmol) and 10 mol% of CuCl at 0°C. The mixture was stirred for 9h at 0°C. Hydrolysis of the reaction mixture with 1N HCl aq gave 1,2-diethyl-3-phenylcyclopentadiene compound **3a** as a mixture of three positional isomers of double bonds. Results are shown in Table 1. Use of CuCN instead of CuCl gave the same results.

Table 1. Preparation of 1,2,3-Trisubstituted Cyclopentadienes and Tetrahydroindene Derivatives by the Reaction of Zirconacyclopentenes with Acid Chlorides in the Presence of a Catalytic Amount of Copper Chloride

Zirconacyclopentene 1			RCOCl	Product	Yield/%^{a}	Ratio of Isomers
R^{1}	**R^{2}**					
Et	Et	**1a**	PhCOCl	**3a**	51 (72)	20:10:1
Et	Et	**1a**	p-$CH_3C_5H_4COCl$	**3b**	(71)	15:5:1
Et	Et	**1a**	2,4-$Cl_2C_5H_3COCl$	**3c**	62 (91)	1:1
Pr	Pr	**1b**	BuCOCl	**3d**	75 (54)	10:6:2:1
Ph	Me	**1c**	PhCOCl	**3e**	35 (66)	5:1
Ph	-	**2a**	PhCOCl	**4a**	54 (63)	-^{b}
Ph	-	**2a**	BuCOCl	**4b**	56 (79)	2:1^{c}
Bu	-	**2b**	PhCOCl	**4c**	55 (98)	-^{b}
Bu	-	**2b**	BuCOCl	**4d**	59 (68)	3:1^{c}

[a] Isolated yields. GC yields are given in parentheses. Products were obtained as a mixture of positional isomers of double bonds. For example, **3a** was obtained as a mixture of three isomers in 20:10:1. The major product was 1-Phenyl-2-ethyl-3-ethylidene-1-cyclopentene. [b] Only one isomer. The structure is shown in eq. (2). [c] Major isomer is shown in eq. (2).

Scheme 1



Reaction of **1** with acid chlorides chemoselectively proceeds at the sp^2 carbon to give **5** as shown in Scheme 1.[5] The carbon attached to either zirconium or copper metal attacks the carbonyl carbon of the complex **5**.[6] Subsequent elimination of a water molecule from **6** after hydrolysis gives 1,2,3-trisubstituted cyclopentadienes **3**. We have recently reported the ring closure of zirconacyclopentanes with acid chlorides in the presence of CuCl. In this reaction the nucleophilic attack of sp^3 carbons to the carbonyl carbon was also observed.[7] However, in the case of zirconacyclopentenes, when phthaloyl chloride was used, the intramolecular Michael addition (Scheme 2)[8] products **9a-d** were obtained in good yields as shown in Table 2. The structure of **9c** was determined by X-ray study;[9] it is shown in Fig. 1.

Scheme 2

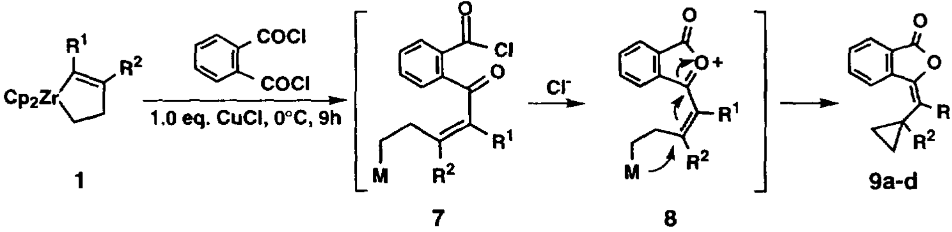


Table 2. Reaction of Zirconacyclopentene with Phthaloyl Chloride in the Presence of CuCl. Formation of Cyclopropylenolate Derivatives.

Zirconacyclopentene 1		Product	Yield[a]/%
R1	R2		
Et	Et	**9a**	65(84)
Pr	Pr	**9b**	60(72)
Ph	Me	**9c**	37(63)
Bu	Bu	**9d**	30(40)

[a] Isolated yields. GC yields are given in parentheses.

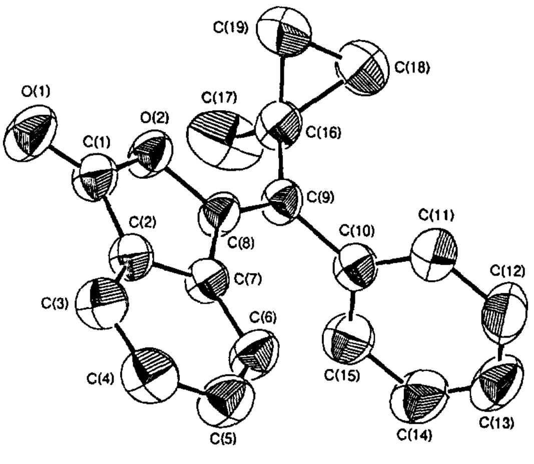


Figure 1. Structure of **9c**

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9. Crystallographic data: fw = 276.3, monoclinic, space group $P2_1/n$, Z = 4, a = 9.587(1) Å, b = 8.182(1) Å, c = 19.553(1) Å, β = 102.82(1)°, V = 1496(2) Å^3, D_x = 1.23 gcm^{-3}, and μ(Cu Kα) = 5.87. Out of the 2911 reflections measured in the range $2° < 2\theta < 140°$, 2531 reflections with $|Fo| > 3\sigma(|Fo|)$ were used for the solution and refinement of the structure. The structure was solved by direct methods (SHELXS-86[10]), and refined by full-matrix least-squares techniques using Xtal3.2[11] software on a Fujitsu S-4/5 workstation. Refinement of positional and thermal parameters led to convergence with R = 0.068, R_w = 0.088.
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