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Journal of Organometallic Chemistry 692 (2007) 5317–5321
Journal of Organometallic Chemistry
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Note

Nucleophilic reactivity of 1-zirconacyclopent-3-ynes: Carbon–carbon bond formation with aldehydes

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Received 15 June 2007; received in revised form 13 July 2007; accepted 24 July 2007
Available online 1 August 2007

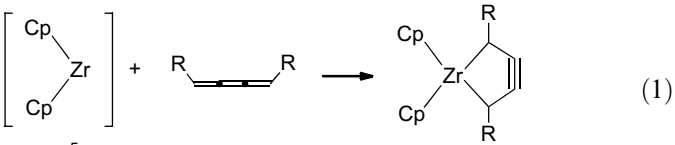
Abstract

Nucleophilic reactions of 1,1-bis(η^5-cyclopentadienyl)-1-zirconacyclopent-3-yne (**1**) with proton and aldehydes were studied. The reaction with HCl gave a mixture of 2-butyne and 1,2-butadiene. Complex **1** reacted with benzaldehyde to give 1-phenyl-2-methyl-2,3-butadien-1-ol (**3**) in moderate yields in the presence of a proton source such as triethylammonium hydrochloride, while it gave 2-methylene-1-phenyl-3-buten-1-ol (**4**) on using triethylammonium tetraphenylborate.

Keywords: Zirconium; Cyclopentyne; Aldehyde; Cycloalkyne

1. Introduction

We recently reported the synthesis and structure of 1-zirconacyclopent-3-yne complexes that could be regarded as isolable five-membered cyclic alkynes (Eq. (1)) [1–3]. 1-Titana- and 1-hafnacyclopent-3-yne complexes were also synthesized [4–6]. These compounds are surprisingly stable despite their strained structure, and pursuing their reactivity is an interesting subject.



$Cp = \eta^5\text{-}C_5H_5$ R = $SiMe_3$, *t*-Bu, H (1)

In the previous study we showed some reactivities of the 1-zirconacyclopent-3-yne complexes. For example, they reacted with low-valent zirconocene to give bimetallic complexes [2,7]. Rosenthal and coworkers reported a Ni-coordinated 1-zirconacyclopent-3-yne [8] and cleavage of its Zr–C bond by a borane compound [9,10]. However, little is known about utilization of these complexes for nucleophilic carbon–carbon bond formation. To the best of our knowledge, insertion of isonitrile into the Zr–C bond in the complex reported by Rosenthal has been the only example to date [11]. Here, we wish to report protonolysis of 1-zirconacyclopent-3-yne compounds and applications to the nucleophilic C–C bond forming reaction.

2. Results and discussion

2.1. Protonolysis of 1-zirconacyclopent-3-ynes

We first examined protonolysis, a reaction with the simplest electrophile, of 1-zirconacyclopenty-3-ne complex **1** (Scheme 1). Our previous study on substituted 1-zirconacyclopent-3-ynes showed that protonolysis by hydrochloric acid gave exclusively 1,4-disubstituted 2-butynes. In this study we found that non-substituted compound **1** exhibited a different reactivity.

A THF solution of **1** was treated with conc. HCl at r.t., and the formation of 2-butyne and 1,2-butadiene in 29%

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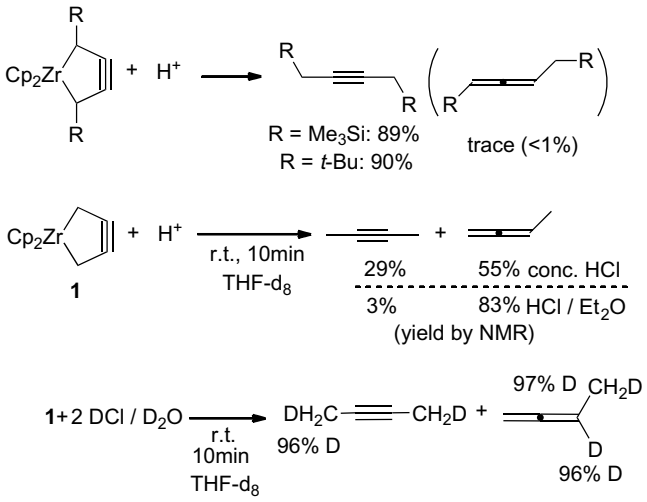
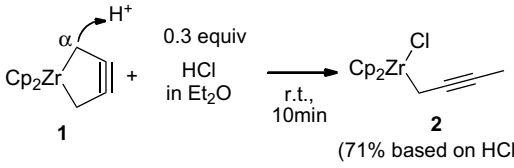
doi:10.1016/j.jorganchem.2007.07.039



Scheme 1. Protonolysis of 1-zirconacyclopent-3-ynes.

and 55% yield, respectively, was observed by NMR spectroscopy. Deuterolysis resulted in incorporation of deuterium at the 1- and 4-positions of 2-butyne and the 3- and 4-positions of 1,2-butadiene. Interestingly, a reaction with anhydrous hydrogen chloride in diethyl ether (1.0 M) gave 1,2-butadiene selectively. These results are contrary to our previous study on the complexes with bulky substituents such as $SiMe_3$ and *t*-Bu groups, where hydrolysis with 1 N HCl exclusively gave 1,4-disubstituted 2-butynes [1].

Since two proton atoms react with **1** to give 2-butyne and 1,2-butadiene, we investigated the first step of the protonolysis in order to shed light on detail of the reaction. When complex **1** was treated with an equimolar amount of HCl/Et_2O, however, only 2-butyne, 1,2-butadiene, Cp_2ZrCl_2 and unreacted **1** were obtained, and no intermediacy was detected. Thus we examined reaction of **1** with 0.3 equiv. of HCl in Et_2O. Protonated species (2-butynyl)chlorozirconocene **2** was observed by NMR spectroscopy (Eq. (2); 71% based on HCl). In the ^1H NMR spectrum a triplet signal at 1.99 ppm and a quartet at 2.75 ppm being coupled by 2.8 Hz appeared; the former was assignable to the methyl group, the latter to the methylene [12].



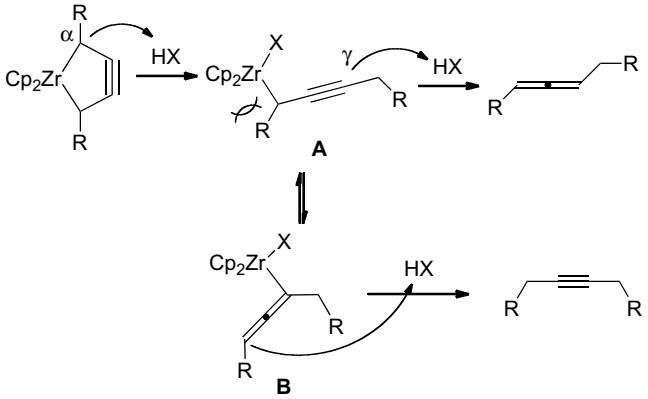
(2)

These results suggest that the second protonation proceeded much faster than the first protonation. In the presence of 1 equiv. of HCl, the intermediate **2** was consumed for the second protonation as soon as it formed. This is in a sharp contrast to the cases of other zirconacyclic compounds in which the second protonolysis is much slower than the first one. It was reported that alcoholysis of zirconacyclopentanes selectively formed alkylalkoxyzirconocene that was inactive for additional alcohol [13,14]. This difference might be due to high reactivity of propargyl intermediate **2** toward electrophiles.

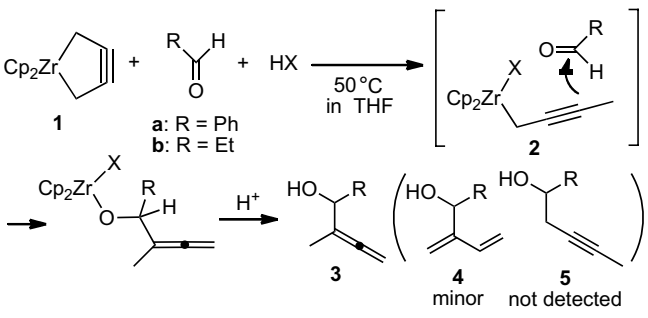
It has been commonly observed on variety of propargyl metal compounds that these species are in equilibrium with allenyl species, and that their nucleophilic attack occurs at the γ-position [15,16]. Also in the present reactions, the second protonation probably occurs at γ-position because **1** reacted with proton under anhydrous conditions to form 2-butynyl species **2** and then gave 1,2-butadiene selectively. Thus the details of protonolysis of 1-zirconacylopent-3-ynes could be described as follows (Scheme 2). The first protonolysis occurred at the α-position of 1-zirconacyclopent-3-yne to afford the 2-butynyl species **A**, where **A** is in equilibrium with **B**. The equilibrium favors **B** for steric reasons if the complex has large R groups. The second protonation proceeds at the γ-position of **A**/**B** more rapidly than the first protonation.

2.2. Nucleophilic reaction with aldehydes

These results prompted us to study nucleophilic attack of **2** on aldehydes. It has been reported that propargylzirconium species react with carbonyl compounds to give β-allenyl alcohols [16]. We added a proton source to the mixture of **1** and benzaldehyde (Scheme 3). After stirring at 50 °C for 1 h, the reaction mixture was hydrolyzed with 1 N HCl to give an allenylated alcohol, 2-methyl-1-phenyl-



Scheme 2. Propargyl and allenyl species in protonolysis.

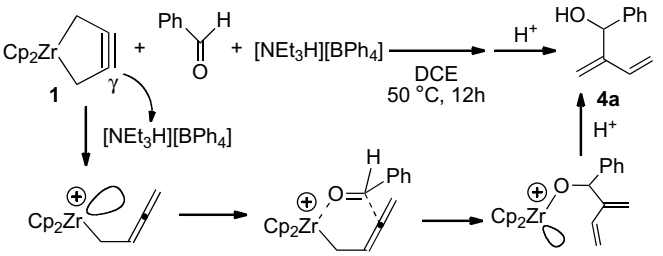


Scheme 3. Reaction of **1** and aldehyde in the presence of HX.

Table 1
Reaction of **1** and benzaldehyde in the presence of various proton sources

Run	HX	Time (h)	Yield of **3a**	**3a**:**4a**
1	None	3	21	94:6
2	H_2O	1	25	>99:1
3	MeOH	1	45	>99:1
4	CH_3COOH	1	28	>99:1
5	$NEt_3 \cdot HCl$	1	52	95:5
6	HCl/Et_2O	2	42	>99:1

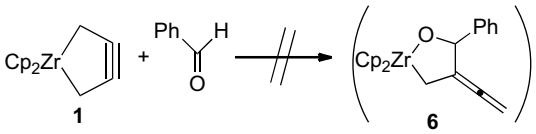
Conditions: 1: benzaldehyde: HX = 1:1:1, 50 °C in THF.



Scheme 4. Plausible mechanism for the formation of **4a**.

2,3-butadien-1-ol (**3a**) in 52% yield. Reactions with various proton sources are shown in Table 1. Triethylammonium hydrochloride was the most effective among them (run 5). It should be noted that the isomeric alcohol, 2-methylene-1-phenyl-3-buten-1-ol (**4a**), was formed as a minor product, although the selectivity was excellent in most cases. 2-Butynylated alcohol **5** was not detected.

Alcohol **3a** was obtained in 21% yield even in the *absence* of any proton sources (run 1). This was probably due to the presence of a trace amount of water in the solvent. Indeed, deuterolysis of the reaction mixture resulted in no deuterium incorporation in the product. This rules out the intermediacy of oxazircona-cyclopentane **6**, at least under these conditions.



(3)

These results showed remarkable stability of **1** toward electrophiles. It is contrary to the facts that 1-zirconacyclopent-3-ene (*s-cis*-1,3-butadiene complex) [17], 1-zirconacyclopent-2-ene [18] and 1-zirconacyclopentane [18] readily react with ketones or aldehydes to give seven-membered oxazirconacycles.

We next examined a variety of ammonium salts as proton sources (Table 2). Most salts gave **3** in moderate to good yields with excellent selectivity. Prolonged reaction time did not improve the yield very much (run 7). Two equivalents of acid resulted in lower yield. Propionaldehyde gave the corresponding alcohol (**3b**), albeit in a low yield. Attempt with other aldehydes such as 2-naphthaldehyde, cinnamaldehyde gave disappointing results as well as ketones and nitriles under these conditions.

To our surprise, reaction with triethylammonium tetraphenylborate in 1,2-dichloroethane resulted in the selective formation of **4a** (run 14). Plausible mechanism for the formation of **4a** in the reaction with $[NEt_3H][BPh_4]$ is depicted in Scheme 4. The first protonolysis occurred at the γ-position for steric reasons to give a cationic 2,3-butadienylzirconium species that reacted with the aldehyde at the γ-position. Our attempt to spectroscopically detect the cationic species in the reaction of **1** and $[NEt_3H][BPh_4]$, however, has been unsuccessful so far.

In conclusion, we showed that the non-substituted 1-zirconacyclopent-3-yne complex **1** reacted with protons to afford 2-butyne and 1,2-butadiene, and that 2-butynylzirconocene was the intermediate species. In the presence of various proton sources, complex **1** reacted with aldehydes to afford allenylated alcohols in moderate yield, while it gave dienylated product using $[NEt_3H][BPh_4]$ as an additive.

3. Experimental

3.1. General

All manipulation was carried out under an inert atmosphere using Schlenk technique or in a glove box. THF was dried over sodium benzophenon ketyl, distilled and stored under argon. 1,2-Dichloroethane was distilled over P_2O_5. Anhydrous hydrogen chloride in diethyl ether

Table 2
Effects of ammonium salts

Run	R	Salts	equiv.	Time (h)	Yield		Ratio
					3	**4**	**3**:**4**
7	Ph	$NEt_3 \cdot HCl$	1	12	59	5	92:8
8	Ph	$NEt_3 \cdot HCl$	2	1	49	2	96:4
9	Ph	$PhNH_2 \cdot HCl$	1	3	67	<1	>99:1
10	Ph	Acetamidine · HCl	1	3	55	2	96:4
11	Ph	n-$BuNH_2 \cdot HCl$	1	3	57	2	96:4
12	Ph	Piperidine · HCl	1	12	47	1	97:3
13	Et	$NEt_3 \cdot HCl$	1	1	24[a]	<1	>99:1
14	Ph	$[NEt_3H][BPh_4]$[b]	1	12	<1	80	< 1:99

[a] 3-Methyl-1,2-hexadien-4-ol (**3b**) was obtained.
[b] In 1,2-dichloroethane.

(1.0 M) was purchased from Aldrich. Benzaldehyde and propionaldehyde was purchased form Kanto Chemical Co., Inc. and distilled. Ammonium salts were purchased and used without further purification. Triethylammonium tetraphenylborate was prepared according to the literature [19]. Complex **1** was prepared by the method reported in our previous paper [2].

3.2. Protonolysis of *1* with hydrochloric acid

To a solution of **1** (54.6 mg, 0.2 mmol) and toluene (20.2 μL, 0.19 mmol) in THF-d_8 (0.4 mL) was added conc.HCl (33 μL, ca. 0.4 mmol) dropwise at r.t. The pale yellow mixture was immediately observed by ^{1}H NMR spectroscopy. The formation of 2-butyne and 1,2-butadiene in 29% and 55%, respectively, was detected. Yields were determined based on toluene as internal standard. Deuterolysis was conducted in a similar manner using DCl/D_2O (20%). Deuterium incorporation was estimated by ^{13}C NMR spectroscopy. 2-Butyne: ^{1}H NMR (THF-d_8): δ 1.60 (s, 6H). ^{13}C NMR (THF-d_8): δ 2.96 (96% D), 74.57. 1,2-butadiene: ^{1}H NMR (THF-d_8): δ 1.52–1.57 (m, 3H), 4.49–4.55 (m, 2H), 4.92–5.04 (m, 1H). ^{13}C NMR (THF-d_8): δ 13.62 (97% D), 74.02, 84.57 (96% D), 209.82.

3.3. Protonolysis of *1* with anhydrous hydrogen chloride

The reaction was carried out similarly to described above using HCl in Et_2O (1.0 M, 0.4 mL, 0.4 mmol). Yields of 2-butyne and 1,2-butadiene were 3% and 83%, respectively.

3.4. Observation of intermediate *2* in protonolysis

Complex **1** (136.6 mg, 0.5 mmol) was dissolved in THF (2.5 mL) and to this solution HCl in Et_2O (1.0 M, 0.15 mL, 0.15 mmol) was added dropwise at 0 °C. Observation by ^{1}H NMR spectroscopy indicated the formation of **2** in 71% based on HCl. Then volatiles were removed *in vacuo* and the yellow residue was dissolved in THF-d_8. **2**: ^{1}H NMR (THF-d_8): δ 1.99 (t, $J = 2.8$ Hz, 3H), 2.75 (q, $J = 2.8$ Hz, 2H), 5.86 (s, 10H). ^{13}C NMR (THF-d_8): δ 9.06 (CH_3), 42.92 (CH_2), 97.98 (q), 102.91 (q), 111.57 (Cp).

3.5. Reaction of *1* with aldehydes in the presence of proton source (preparation of *3*)

Typically, to a solution of **1** (27.3 mg, 0.1 mmol) in THF (1 mL) were added benzaldehyde (10.6 mg, 0.1 mmol) and triethylamine hydrochloride (13.8 mg, 0.1 mmol) at r.t. After stirring at 50 °C for 1 h, 1 N HCl was added to quench the reaction. Yield was determined by gas chromatography. To isolate the product, complex **1** was prepared *in situ* using 10 mmol of Cp_2ZrCl_2, and the reaction was conducted in a similar manner. After dil.HCl was added, the mixture was extracted with ether and the organic layer was dried with $MgSO_4$, then volatiles were removed *in vacuo* leaving a pale yellow oil. The product was purified by column chromatography (silica gel, hexane/EtOAc = 95/5). Yield 48% isolated. The products were identified according to the literature [20,21].

3.6. Reaction of *1* with aldehydes in the presence of $[NEt_3H][BPh_4]$ (preparation of *4a*)

The reaction was conducted similarly to the above described using triethylammonium tetraphenylborate and 1,2-dichloroethane. For isolation of the product, complex **1** (683.1 mg, 2.5 mmol), benzaldehyde (239 mg, 2.25 mmol), triethylammonium tetraphenylborate (1.05 g, 2.5 mmol) and 12 mL of 1,2-dichloroethane was used. To the reaction mixture was added 1 N HCl and extracted with chloroform, dried over $MgSO_4$ and purified by column chromatography (silica gel, hexane/EtOAc = 95/5). Yield was determined by gas chromatography (80%). The product was identified based on the reported spectroscopic data [22].

Acknowledgement

This work was financially supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Grant-in-Aid for Scientific Research, C: No. 18550065).

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