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A half cleaved zirconacyclopentadiene ☆

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Abstract

When the sterically strained bicyclic zirconacyclopentadiene **2** is reacted with two equivalents of iodine in the presence of copper(I) chloride, the diiodinated product **4** forms in the range of 10 h. However, when reacted only for 2 h, the monoiodinated zirconium complex **3** is isolated. **3** shows an unexpected stability towards hydrolysis and oxidation. The molecular structure of complex **3** has been determined by X-ray structural analysis.

Keywords: Zirconacyclopentadienes; Half Cleavage; Alkenylzirconocenes; Alkenyliodides

1. Introduction

Bis(cyclopentadienyl)zirconium(IV) complexes were discovered almost half a century ago, but their applications in organic and polymer chemistry continue to expand at a rapid pace [1]. Processes such as hydrozirconation, carbozirconation, transmetallations and bond insertions open up a wide range of different gateways towards these zirconocene derivatives.

As 1,4-dianion precursors, zirconacyclopentadienes are especially valuable. Using the Negishi reagent Cp_2Zr(butene), they can be easily prepared from two alkynes in a one pot synthesis [2] (Scheme 1).

Treatment of these zirconacycles with iodine, NCS or NBS results in the oxidative cleavage of the carbon–zirconium bonds [3]. The first bond reacts generally much faster and to achieve full conversion to, e.g., the diiodinated butadienes either a large excess of iodine and long reaction times are required, or the reactions are catalyzed with copper(I) chloride [3a]. With no catalyst or only one equivalent of I_2, NCS or NBS the monohalogenated butadienes are produced and have been successfully used in situ for further reactions as described by Takahashi et al. [3] (Scheme 2).

There are no reports of any attempts to isolate the intermediate half cleaved zirconium complexes, implying that these compounds may be either quite sensitive compounds or that they are thermally unstable, as may be concluded from the formation of cyclobutadienes upon treatment with CuCl [3d]. This contribution will present the first successful isolated half cleaved zirconium complex of this kind.

2. Results and discussion

In an attempt to synthesize an 1,4-bisiodobutadiene with an anellated cyclohexyl backbone, the sterically strained bicyclic zirconacyclopentadiene **2** was reacted with two equivalents of iodine in the presence of copper(I) chloride. In contrast to reactions with less strained zirconacyclopentadienes [4], the diiodinated product **4** was only isolated after prolonged reaction times in the range of 10 h. When reacted only for 2 h, the monoiodinated product **3** was isolated as the only product by aqueous workup with sodium thiosulfate and extraction with ether as yellow air stable crystals (Scheme 3).

The halogen atom at the zirconium center has been unambiguously assigned as a chlorine atom by X-ray structural analysis and an exchange of the iodine atom must have taken place after the cleavage reaction

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☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2003.10.039.

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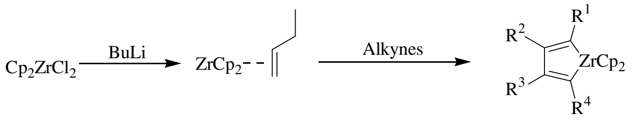
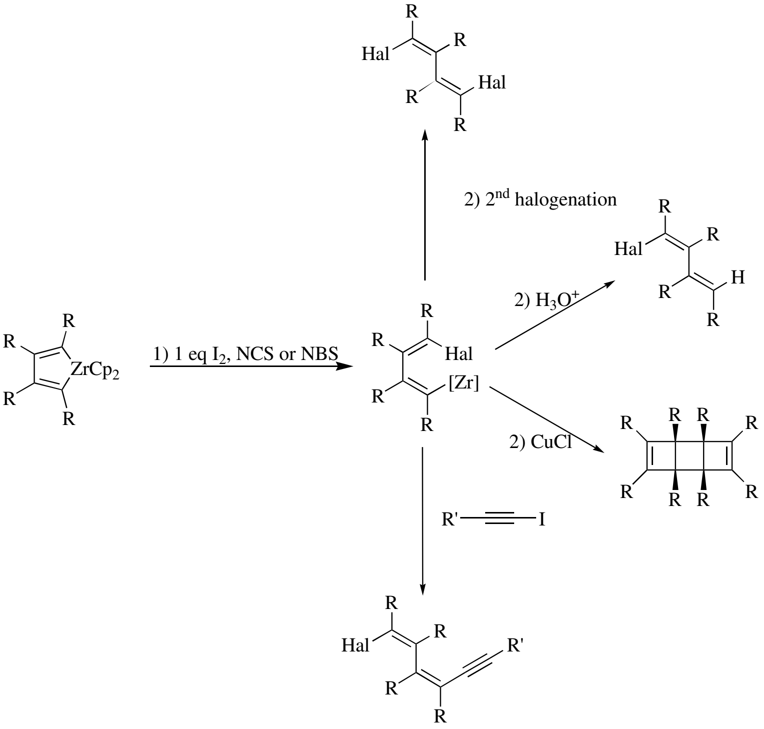


Scheme 1.

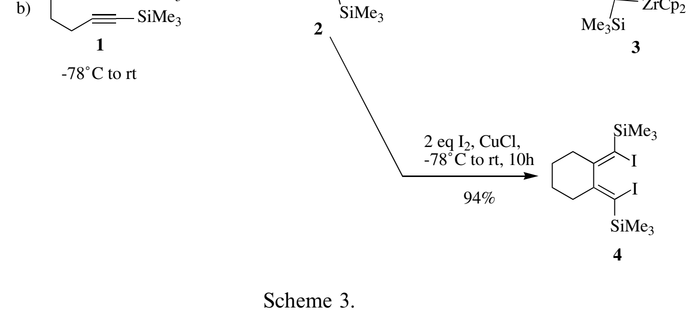
(see Table 1). Similar halogen exchange reactions have been observed by Erker and co-workers [5] for related alkenylzirconocene complexes, and, taking the strained *cis* conformation of the butadiene unit into account, the driving force for the exchange will be not only the formation of the stronger Zr–Cl bond but also relief of steric strain.

With no previous reports of any isolated half cleaved zirconacyclopentadienes, the pronounced stability of zirconium complex **3** is unexpected and its stability towards water and air during workup needs some discussion.

To some extend the stability of **3** can be explained by the sterical shielding effect of the large substituents surrounding the remaining carbon–zirconium bond. As can be seen in the solid state structure (Fig. 1), this bond is effectively enclosed by the cyclopentadienyl rings, the bulky trimethylsilyl groups and the anellated cyclohexyl ring. The presence of these bulky substituents may as well further stabilize the complex towards reductive elimination to form a cyclobutadiene derivative in the



Scheme 2.



Scheme 3.

Table 1
Selected bond lengths (Å) and angles (deg) for **3**

Zr–Cl	2.4502(6)
Zr–C1	2.3286(17)
C1–C2	1.345(2)
C2–C3	1.504(2)
C3–C4	1.337(2)
C4–I	2.1632(17)
Zr–C1–C2	121.13(13)
Zr–C1–Si1	124.34(9)
Si1–C1–C2	114.49(13)
C1–C2–C3	126.14(16)
C1–C2–C8	127.88(17)
C8–C2–C3	105.46(15)
C2–C3–C4	124.78(16)
C2–C3–C5	111.08(15)
C5–C3–C4	122.38(17)
C3–C4–I	116.14(13)
Si2–C4–I	108.64(8)
C3–C4–Si2	135.22(14)

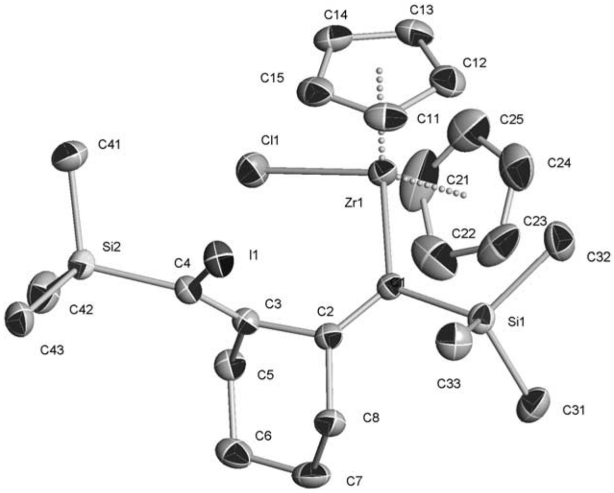


Fig. 1. View of the molecular structure of **3** (50% probability ellipsoids).

presence of CuCl, as it has been observed for other less sterically shielded complexes [3d].

On the other side, the replacement of the original iodine atom at the zirconium indicates, that the metal center is not totally inaccessible for further reactions. Therefore, the insensitivity towards oxidation and hydrolysis seems to be at least in part due to some inherent stability of the complex itself. This assumption seems to be further confirmed by the considerable strain, which is present in the molecule. The sterical demands of the Cp_2ZrCl moiety and the iodine atom are forcing the two double bonds out of conjugation with the dihedral angle being as large as 91.53°. The angles around the carbon atoms C2 and C3 are differing considerably from the idealized 120°. With 105.46° the angle C3–C2–C8 exhibits the most extreme deviation. Due to this steric strain, the carbon–zirconium bond is expected to be considerably weakened. Indeed, the Zr–C bond length is with 2.3286(17) Å rather long when compared with those of other alkenylzirconocene complexes, which are generally in the range of 2.209–2.258 Å [5]. The bond length found here compares better with weaker carbon–zirconium bonds as they are found in complexes having an additional donor ligand such as an amine or phosphine [6]. Therefore, replacement of the Cp_2ZrCl moiety by hydrolysis should lead to much less strained molecule. In contrast to that, the molecule is stable during aqueous workup, implying an inherent stability of the complex not derived from sterical protection alone.

Taking into account, that zirconacyclopentadienes are easily synthesized in a one pot synthesis from readily available alkynes, and that they have two functional groups of opposite polarity, the surprising stability of the complex presented here should be taken as a strong encouragement for further investigations of this class of compounds. Especially if the zirconium complexes can be isolated as pure materials rather than used in situ these compounds may well find a much more extended use in organic synthesis than possible with the present in situ methods.

3. Experimental

3.1. 1,2-Bis(trimethylsilyl)octa-1,7-diyne (**1**)

1 was synthesized as described for 1,2-bis(trimethylstannyl)octa-1,7-diyne [7]. **1** is distilled at 155–165 mTorr/58–65 °C to get 85% of the product as a clear liquid, that solidifies slowly at 4 °C. ^{1}H NMR (299.858 MHz, $CDCl_3$, rt): $\delta = 0.157$ (s, 18H, $SiMe_3$), 1.385 (m, 4H, CH_2), 1.935 (m, 4H, CH_2).

3.2. 1,6-Bis(iodotrimethylsilylmethylene)cyclohexane (**4**)

To a THF solution (100 ml) of Cp_2ZrCl_2 (2.5 g, 8.55 mmol) and **1** (2.14 g, 8.54 mmol), is added a hexane solution of *n*-BuLi (6.1 ml, 2.8 M, 17.08 mmol) at −78 °C. After stirring for 30 min, the mixture is allowed to warm up to room temperature and is stirred for 4 h. A THF solution (100 ml) of iodine (5 g, 19.5 mmol) and solid Cu(I)Cl (0.853 g, 8.54 mmol) are added at −78 °C. After warming up to room temperature the mixture is stirred for further 10 h. A saturated aqueous solution of $Na_2S_2O_3$ is added and the mixture is extracted with pentanes. The combined extracts are washed with brine, dried over $MgSO_4$, filtered through a bed of celite and condensed by rotary evaporation. Recrystallization from pentanes at −30 °C yields **4** (4.06 g, 8.06 mmol, 94%). ^{1}H NMR (299.858 MHz, $CDCl_3$): $\delta = 0.325$ (s, 18H, $SiMe_3$), 1.26 (m, 2H, CH_2), 1.5 (m, 2H, CH_2), 2.09 (m, 2H, CH_2), 2.73 (m, 2H, CH_2).

3.3. 1-(iodotrimethylsilylmethylene)-6-{(chloro-di-η^5-cyclopentadienyl-zirconium)trimethylsilylmethylene} cyclohexane (**3**)

As for **4**, but the iodination reaction is stopped after 2 h at room temperature by addition of aqueous sodium thiosulfate. The organic layer is extracted with ether, the ether fractions are dried with $MgSO_4$, and filtered through a bed of celite. Upon concentration of the ethereal solution and cooling to 4 °C, **3** is isolated as bright yellow crystals (4.6 g, 7.26 mmol, 85%). ^1H NMR (399.905 MHz, $CDCl_3$, rt): $\delta = 6.377$ (s, 5H, Cp), 6.272 (s, 5H, Cp), 2.756 (m, 2H, CH_2), 2.254 (m, 2H, CH_2),1.891 (m, 2H, CH_2), 1.470 (m, 2H, CH_2),0.299 (s, 9H, CH_3), 0.291 (s, 9H, CH_3); ^{13}C NMR (100.565 MHz, $CDCl_3$): $\delta = 180.917$ (=C), 168.027 (=C), 165.941 (=C), 113.091 (Cp), 112.818 (Cp), 103.683 (=C), 43.329 (CH_2), 39.418 (CH_2), 31.695 (CH_2), 30.235 (CH_2), 4.656 (CH_3), 1.651 (CH_3). Anal. calcd. for ($C_{24}H_{36}Si_2ZrClI$): C 45.45, H 5.72, total halogen (as Cl) 11.18. Found: C 45.31, H 5.67 total halogen (as Cl) 11.25.

Crystallographic data were collected on a Bruker AXS SMART APEX CCD diffractometer using monochromated Mo Kα-radiation. The structure was solved using direct methods and refined using SHELXL programs [8]. $C_{24}H_{36}ClISi_2Zr$; $M = 634.28$, monoclinic, $P2_1/c$; $a = 16.9457(9)$ Å, $b = 10.2028(5)$ Å, $c = 17.0279(9)$ Å; $\beta = 111.5130(10)°$, $Z = 4$, 293(2) K, R(all reflections) = 0.0285.

Supplementary material

Supplementary crystallographic data for **3** have been deposited as "CCDC-220957" with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1UEZ, UK; fax: +44(0)1223-336033, e-mail: deposit@ccdc.cam.ac.uk].

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