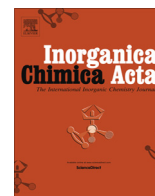




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: [www.elsevier.com/locate/ica](http://www.elsevier.com/locate/ica)

Research paper

## Early transition metal and lanthanide metallocenes bearing dihydroazulenide ligands

Joachim Richter<sup>a</sup>, Phil Liebing<sup>b</sup>, Frank T. Edelmann<sup>b,\*</sup><sup>a</sup> Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstr 4, D-37077 Göttingen, Germany<sup>b</sup> Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany

## ARTICLE INFO

## Article history:

Received 22 April 2017

Received in revised form 1 June 2017

Accepted 7 June 2017

Available online xxx

Dedicated to a great chemist and friend, Professor Ionel Haiduc, on the occasion of his 80th birthday

## Keywords:

Azulene

Guaiazulene

Lithium

Zirconium

Metallocenes

## ABSTRACT

A generally applicable synthetic protocol for preparing early transition metal and lanthanide metallocenes bearing dihydroazulenide ligands has been developed. Lithium dihydroazulenide precursors such as lithium 4-methyldihydroazulenide (**2**, = LiC<sub>11</sub>H<sub>11</sub>), lithium 7-isopropyl-1,4,8-trimethyldihydroazulenide (**4**, = LiC<sub>16</sub>H<sub>21</sub>), and lithium 7-isopropyl-1,4-dimethyl-8-phenyldihydroazulenide (**5**, = LiC<sub>21</sub>H<sub>23</sub>) were prepared by treatment of azulene or guaiazulene with methyllithium or phenyllithium, resp. While variable-temperature <sup>7</sup>Li NMR revealed the presence of monomeric and dimeric structures in solution, an X-ray diffraction study of the DME adduct LiC<sub>16</sub>H<sub>21</sub>(DME) (**4a**) showed a monomer with η<sup>5</sup>-coordination of the azulene-derived ligand in the solid state. Reactions of MCl<sub>4</sub>(THF)<sub>2</sub> (M = Ti, Zr) with 2 equivalents of the lithium dihydroazulenides in THF solution provided the Ti and Zr metallocenes **6–11** as inseparable mixtures of stereoisomers. However, pure products could be isolated by introducing only one dihydroazulenide ligand as in the mixed-ligand zirconium sandwich complexes (C<sub>5</sub>Me<sub>5</sub>)(C<sub>11</sub>H<sub>11</sub>)ZrCl<sub>2</sub> (**12A**) and (C<sub>5</sub>Me<sub>5</sub>)(guaiazulenide)ZrCl<sub>2</sub> (**13**). In contrast, two related neodymium(III) sandwich complexes containing dihydroazulenide ligands (**14**, **15**) also formed mixtures of stereoisomers.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

Metallocene catalysts of titanium, zirconium, and hafnium play a central role in polyolefin production [1]. Among the most active catalysts of this type are metallocenes and *ansa*-metallocenes bearing indenyl and fluorenyl ligands in which the cyclopentadienyl moiety is fused to one or two benzene rings. Much less is known about related complexes containing a seven-membered ring attached to cyclopentadienyl, e.g. azulene-based ligand systems. For example, a general synthesis and metal complexes of fused-ring bicyclic cyclopentadienes have been reported by Herrmann et al. in 1993 [2]. In this study, cyclopentadienes possessing fused hydrocarbon (CH<sub>2</sub>)<sub>n</sub> chains have been prepared by rearrangement of spiro-lactones. The latter compounds were made from commercially available oxiranes in a three-step procedure. Cyclopentadienes containing five- and six-membered alkylidene groups, -(CH<sub>2</sub>)<sub>5</sub>- and -(CH)<sub>4</sub>-, respectively, in 1,2-positions were thus prepared and used as ligands for novel neodymium and zirconium complexes. However, ligands incorporating a seven-membered ring were not included [2]. In 1989, Brintzinger et al. reported the synthesis and structural characterization of the first

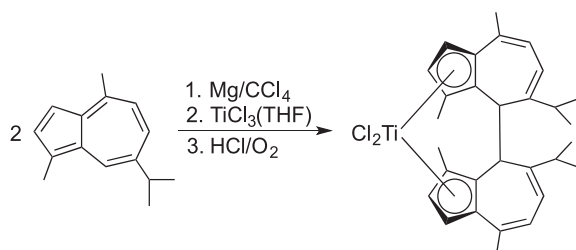
azulene-derived *ansa*-metallocene derivative of titanium. It was found that the product of an Mg/CCl<sub>4</sub>-induced reductive coupling of guaiazulene (=7-isopropyl-1,4-dimethylazulene) reacted with TiCl<sub>3</sub>·3THF to yield, after oxidation with HCl/O<sub>2</sub>, the new *ansa*-titanocene complex *R,S*-8,8'-biguaiazulenide titanium dichloride, which contains a C–C bond between its two guaiazulenide ligand moieties (Scheme 1) [3].

The chemistry of azulene-based Group 4 metal *ansa*-metallocenes has been further expanded by Iwama and co-workers. These researchers succeeded in the design of bridging bis(dihydroazulenyl) ligands and used them to prepare a series of novel *ansa*-bis(dihydroazulenyl) and bis(tetrahydroazulenyl) metallocenes of zirconium and hafnium. A typical preparative route to such a bridged bis(dihydroazulenyl) ligand e.g. involves treatment of 2-methylazulene with methyllithium to give the corresponding lithium dihydroazulenide, which is followed by coupling with dichlorodimethylsilane. Subsequent lithiation and reaction with ZrCl<sub>4</sub> or HfCl<sub>4</sub> gave the desired *ansa*-zirconocenes or -hafnocenes. Hydrogenation of the unsaturated seven-membered rings afforded the corresponding bis(tetrahydroazulenyl) complexes [4].

In organolanthanide chemistry, compounds containing azulene-derived ligands are exceedingly rare. In 2003, Fedushkin et al. reported the synthesis of two divalent *ansa*-ytterbocenes via reductive dimerization of guaiazulene upon reaction with

\* Corresponding author.

E-mail address: [frank.edelmann@ovgu.de](mailto:frank.edelmann@ovgu.de) (F.T. Edelmann).



**Scheme 1.** Synthesis of *R,S*-8,8'-biguaiazulenide titanium dichloride [3].

ytterbium naphthalenide in THF. The compounds  $(C_{15}H_{18})_2Yb(NC_5H_5)_2$  and  $(C_{15}H_{18})_2Yb(THF)_2$  ( $C_{15}H_{18}$  = guaiazulen-8-yl) were structurally characterized by X-ray diffraction [5]. The same authors also reported the first metal complex coordinated by an azulene dianion. The lutetium complex  $CpLu(2\eta^1:\eta^2-C_{15}H_{18})(DME)$  ( $C_{15}H_{18}^{2-}$  = dianion of guaiazulene) was prepared by reduction of guaiazulene with the lutetium naphthalenide complex  $CpLu(2\eta^1:\eta^2-C_{10}H_8)(DME)$  in 1,2-dimethoxyethane (DME). The molecule has an unusual skewed *pseudo*-sandwich structure in which the Lu atom is  $\eta^5$ -coordinated by the cyclopentadienyl ring and  $2\eta^1:\eta^2$ -coordinated by the seven-membered ring of the guaiazulenide ligand [6].

Apparently, the initial products obtained by addition of organolithium compounds to azulenes, *i.e.* the lithium dihydroazulenides, have not been employed as precursors for new metallocenes. We report here a straightforward and generally applicable synthetic protocol leading to group 4 and rare-earth metal metallocenes containing dihydroazulenide ligands.

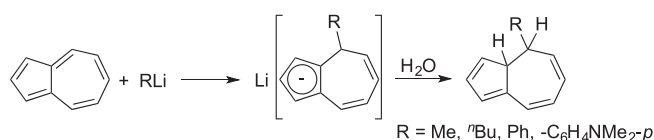
## 2. Results and discussion

### 2.1. Synthesis and structure of lithium dihydroazulenides

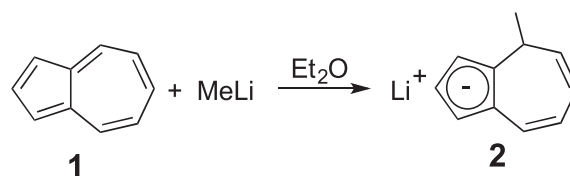
As early as 1957, in the course of their pioneering work on azulene chemistry, Hafner et al. found that azulenes readily add organolithium compounds under formation of the corresponding lithium dihydroazulenides, which were isolated as solvates with diethyl ether. Reactions of azulene with MeLi,  $n$ BuLi, PhLi and *p*-LiC<sub>6</sub>H<sub>4</sub>-NMe<sub>2</sub> were studied. Subsequent hydrolysis afforded the thermally labile 4-substituted dihydroazulenes (Scheme 2). Dehydration of the latter opened up a synthetic route to the corresponding 4-substituted azulenes [7].

This reaction is analogous to the nucleophilic addition of lithium alkyls across the exocyclic double bond of pentafulvenes, which affords substituted lithium cyclopentadienides [8]. This “fulvene route” has become one of the most effective synthetic pathways to substituted cyclopentadienide anions and the corresponding metallocenes [9]. For the reaction of the parent azulene (1) with methyllithium we essentially followed the original route published by Hafner et al. [7]. Treatment of 1 with 1 equiv. of methyllithium in diethyl ether according to Scheme 3 cleanly afforded lithium 4-methyldihydroazulenide (2).

The reaction was easily followed by the disappearance of the dark blue color of azulene. The original preparation was slightly



**Scheme 2.** Synthesis of 4-substituted dihydroazulenes according to Hafner et al. [7].

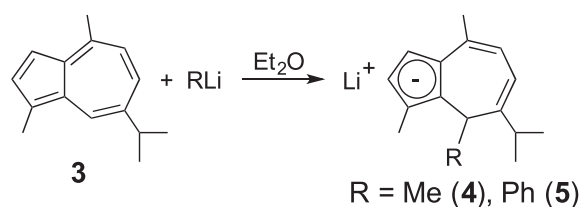


**Scheme 3.** Preparation of lithium 4-methyldihydroazulenide (2, = LiC<sub>11</sub>H<sub>11</sub>).

modified in the way that the precipitated product was not washed with diethyl ether but with *n*-pentane to afford the unsolvated lithium salt 2 as off-white, very air-sensitive microcrystalline solid in 76% yield. The compound was fully characterized by its NMR (<sup>1</sup>H, <sup>13</sup>C), IR, and MS data as well as elemental analysis. In the <sup>1</sup>H NMR spectrum, the proton at the  $sp^3$ -hybridized carbon atom in the seven-membered ring (H4) was observed as a multiplet at  $\delta$  3.15. A doublet at  $\delta$  1.22 ( $^3J_{H-H}$  = 7.0 Hz) could be assigned to the methyl substituent. The corresponding signals in the <sup>13</sup>C NMR spectrum appeared at  $\delta$  35.0 (C4) and  $\delta$  26.7 (CH<sub>3</sub>), respectively.

Perhaps the most attractive azulene precursor is the naturally occurring guaiazulene (3, = 7-isopropyl-1,4-dimethylazulene) which is the blue constituent of some essential oils, mainly oil of guaiac and chamomile oil. These oils also serve as its commercial sources, making guaiazulene the cheapest commercially available azulene derivative. We found that the organolithium addition can also be performed successfully with guaiazulene. As illustrated in Scheme 4, methyllithium and phenyllithium could be added to 3 to afford the corresponding lithium dihydroazulenides 4 (R = Me) and 5 (R = Ph) in high yields (4: 85%, 5: 80%).

Lithium 7-isopropyl-1,4,8-trimethyldihydroazulenide (4) was isolated as a pale greenish, very air- and moisture-sensitive solid. Notable was the formation of significant amounts of oily by-products in this reaction. These could, however, be completely removed by Soxhlet extraction of the crude product with *n*-pentane. This purification procedure once again afforded the unsolvated product, which could be fully characterized by the usual combination of elemental analysis and spectroscopic data. In the <sup>1</sup>H NMR spectrum of 4 a doublet at  $\delta$  0.87 ppm could be assigned to the added methyl group, while the proton on the  $sp^3$ -hybridized carbon atom C8 gave rise to a quartet at  $\delta$  3.49 ppm ( $^3J_{H-H}$  = 7.0 Hz). The corresponding signals in the <sup>13</sup>C NMR spectrum were observed at  $\delta$  19.1 ppm (CH<sub>3</sub>) and  $\delta$  34.5 ppm (C8), respectively. The 8-phenyl-substituted lithium dihydroazulenide 5 was isolated in the same manner as an air-sensitive, yellow solid. In this case, the reaction was cleaner than that with MeLi, and no further purification by Soxhlet extraction was necessary. The <sup>1</sup>H NMR spectrum of 5 showed multiplets around  $\delta$  6.95 ppm for the added phenyl group and a singlet at  $\delta$  4.72 ppm for the proton at C8. As expected, all three isolated lithium dihydroazulenides 2, 4, and 5 are highly sensitive to air and moisture. They dissolve freely in THF or DME (=1,2-dimethoxyethane), but have a low solubility in diethyl ether and are virtually insoluble in aromatic or aliphatic hydrocarbon solvents.



**Scheme 4.** Preparation of lithium 7-isopropyl-1,4,8-trimethyldihydroazulenide (4, = LiC<sub>16</sub>H<sub>21</sub>), and lithium 7-isopropyl-1,4-dimethyl-8-phenyldihydroazulenide (5, = LiC<sub>21</sub>H<sub>23</sub>).

Download English Version:

<https://daneshyari.com/en/article/7750567>

Download Persian Version:

<https://daneshyari.com/article/7750567>

[Daneshyari.com](https://daneshyari.com)