SOME REACTIONS OF THE PRODUCTS OF REACTIONS OF 1,4-BIS(TRIMETHYLSILYL)-1,3-BUTADIYNE WITH TITANOCENE AND ZIRCONOCENE

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Bis(η^5-cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene (**1**) and the seven-membered zirconacyclocumulene bis(η^5-cyclopentadienyl)-2,4,7-tris(trimethylsilyl)-3-(trimethylsilylethynyl) zirconacyclohepta-2,4,5,6-tetraene (**2**) react with sulfur monochloride to yield an identical product, 2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)thiophene (**3**). A one-to-one mixture of the homo- and heterobimetallic bis-σ,π-acetylide bridged complexes $Cp_2Ti(\mu\text{-}\eta^1:\eta^2\text{-}C\equiv CSiMe_3)M(\mu\text{-}\eta^1:\eta^2\text{-}C\equiv CSiMe_3)Cp_2$ (M = Zr (**4**), M = Ti (**5**)) is formed in the reaction of zirconacyclocumulene **2** with three equivalents of $Cp_2Ti(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$. The reaction proceeds most likely *via* alkyne elimination, a C–C-single bond activation, and the cleavage of the starting diyne takes place.

Key words: Metallocenes; Butadiyne; C–C-Single bond activation; Thiophene.

In the modern chemistry of acetylene[1] with Group 4 metallocene complexes, great research activity is directed to diynes[2–9]. Recently we have found metallocene complexes of bis(trimethylsilyl)acetylene to be excellent organometallic reagents for the generation[10] of titanocene and zirconocene moieties Cp_2M (M = Ti, Zr). In their reactions with 1,4-bis(trimethylsilyl)butadiyne, bis(η^5-cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene[11] (**1**) and the seven-membered zirconacyclocumulene[4,12] bis(η^5-cyclopentadienyl)-2,4,7-tris(trimethylsilyl)-3-(trimethylsilylethynyl)zirconacyclohepta-2,4,5,6-tetraene (**2**) are formed, respectively. It was assumed that an analogous zirconacyclopentadiene is an intermediate in formation of the

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seven membered zirconacyclocumulene **2** which is formed *via* insertion of the α-acetylide group into the zirconacyclopentadiene. On the other hand, also the insertion of the diyne into a five membered zirconacyclocumulene[12] seemed to be possible as well[10].

To understand the different bonding situation and stability of such titanacyclopentadienes and seven-membered zirconacyclocumulenes we made use of several selected chemical reactions. In this paper we describe the interaction of both complexes with sulfur monochloride as well as the reaction of the zirconium complex **2** with three equivalents of the titanocene $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$.

EXPERIMENTAL

General

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus; X-ray diffraction data were collected on a STOE-IPDS diffractometer using MoKα radiation. The structures were solved by direct methods[13a] (SHELXS86) and refined by full-matrix least-square techniques against F^2 (ref.[13b]); structural representation: Schakal-92; (E. Keller, University of Freiburg).

Supplementary material. Tables of crystal structure, details of data collection, bond angles, distances and atomic positional and thermal parameters of **4**; observed and calculated structure factors of **4**. Ordering information is given on any current masthead page.

Synthesis of Compounds **3–5**

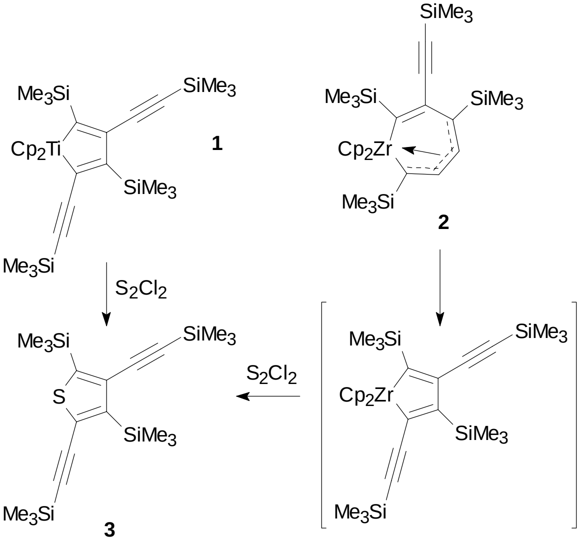
A) Preparation of **3** *starting from* **1**: A total of 0.265 g (0.47 mmol) of complex **1** was dissolved in THF (10 ml), and sulfur monochloride (0.04 ml, 0.5 mmol) was added to the red solution. The mixture was stirred at 55 °C for 6 h, the red-brown solution was evaporated to dryness, and the residue was extracted with (4 × 3 ml) of hexane. The hexane solution was purified by flash chromatography (8 × 2 cm) on activity III alumina to yield 0.098 g (49.7%) of **3** as a pale yellow liquid.

B) Starting from **2**: A total of 0.726 g (1.19 mmol) of complex **2** was dissolved in THF (20 ml), and sulfur monochloride (0.1 ml, 1.25 mmol) was added to the yellow solution. The mixture was stirred at 55 °C for 1 h, the red-brown solution was evaporated to dryness, and the residue was extracted with (3 × 10 ml) of hexane. The hexane solution was purified by flash chromatography (9 × 2 cm) on activity III alumina to yield 0.102 g (20.4%) of **3** as a pale yellow liquid. IR spectrum (Nujol mull): 2 148 cm^{-1} (ν(C≡C)); 1 249 cm^{-1} (δ(Si–Me)); ^1H NMR spectrum (C_6D_6; δ, ppm): 0.20 s, 9 H ($SiMe_3$); 0.23 s, 9 H ($SiMe_3$); 0.35 s, 9 H ($SiMe_3$); 0.61 s, 9 H ($SiMe_3$); ^{13}C NMR spectrum (C_6D_6; δ, ppm): –0.90, –0.42, –0.39, +0.22 ($SiMe_3$); 97.5, 99.8, 102.2, 104.2 (C≡C); 133.8, 134.3, 148.4, 148.7 (Cβ and Cα); GC-MS (*m*/*z*, 70 eV): 420 $[M]^+$.

Preparation of **4** *and* **5**. A total of 0.405 g (0.66 mmol) of complex **2** and $Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$ (0.698 g, 2.00 mmol) were dissolved in hexane (15 ml). The yellow mixture was stirred at 55 °C for 25 h to change the color to dark red. The warm solution was filtered and allowed to crystallize at 20 °C. After one day red crystals containing **4** and **5** in a one-to-one ratio were obtained. The crystals were washed with cold hexane and dried *in vacuo* to give 0.295 g (38.9%) of a one-to-one mixture of **4** and **5**, m.p. 228–229 °C. For **4** with **5** $C_{30}H_{38}Si_2Ti_{1.5}Zr_{0.5}$ (572.2) calculated: 62.97% C, 6.69% H; found: 62.38% C, 6.25% H. IR spectrum of **4** (Nujol mull): 1 759, 1 833 cm^{-1} (ν(C≡C)); ^{1}H NMR spectrum of **4** (TDF; δ, ppm): 0.43 s, 18 H ($SiMe_3$); 5.05 s, 10 H (Cp); 5.38 s, 10 H (Cp); ^{13}C NMR spectrum of **4** (TDF; δ, ppm): 2.1 ($SiMe_3$); 101.2 (Cp); 105.5 (Cp); Cβ and Cα were not observed at 20 °C; mass spectrum of **4** and **5** (*m/z*, 70 eV): 592 $[M(\mathbf{4})]^+$, 550 $[M(\mathbf{5})]^+$, 317 $[Cp_2Zr–C≡CSiMe_3]^+$; 275 $[Cp_2Ti–C≡CSiMe_3]^+$; 220 $[Cp_2Zr]^+$; 178 $[Cp_2Ti]^+$.

RESULTS AND DISCUSSION

The reactions of bis(η^5-cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene (**1**) and the seven-membered zirconacyclocumulene bis(η^5-cyclopentadienyl)-2,4,7-tris(trimethylsilyl)-3-(trimethylsilylethynyl)zirconacyclohepta-2,4,5,6-tetraene (**2**) with sulfur monochloride give an identical product, 2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)thiophene (**3**) (Scheme 1).



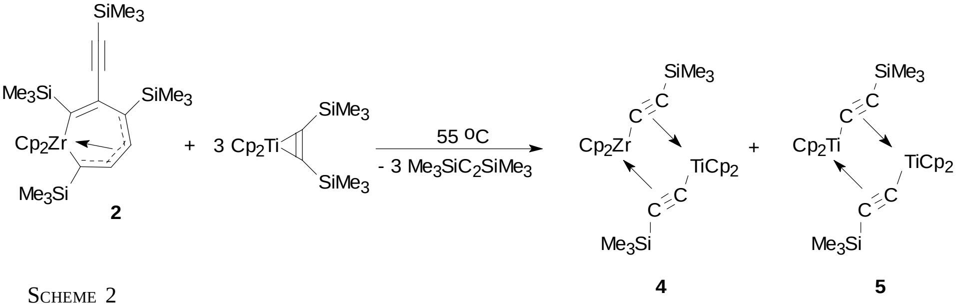
SCHEME 1

Such a reaction is not unusual and was well established in the case of simple substituted metallacyclopentadiene complexes[14]. However, in the case of polyfunctional coupling products like **1** and **2**, it is interesting for three reasons.

First, the clean coupling reaction of the diynes yields only the single regioisomer with trimethylsilyl groups in the α- and β-position to the metal. Second, protodesilylation[15] of the obtained thiophenes can open the way to products that are impossible to prepare by regioselective coupling of mono- or unsubstituted diacetylenes. Third, derivatization of the remaining two free triple bonds may be regarded as a strategy towards the synthesis of new heterocyclic compounds.

Surprisingly, the reaction of **2** with S_2Cl_2 gives **3**, too. As for a reaction pathway, a ring contraction of zirconacyclocumulene 2 in solution to a zirconacyclopentadiene complex (an analogue to **1**) is assumed.

Three equivalents of the titanocene source[16] $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}SiMe_3)$ react with the seven membered zirconacyclocumulene **2** to give a one-to-one mixture of the homo- and the heterobimetallic bis-σ,π-acetylide bridged complexes[17] $Cp_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)M(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)Cp_2$, where M = Zr for **4** and M = Ti for **5** (Scheme 2).



SCHEME 2

The complexes of this type are well-known. One part of the mixture, the homobimetallic titanium species $Cp_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{- }C{\equiv}CSiMe_3)Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)Cp_2$ (**5**) was described some years ago in a salt elimination reaction[18] starting from Cp_2TiCl, in the reductive elimination of bis(trimethylsilyl)butadiyne[19,20] from $Cp_2Ti(C{\equiv}CSiMe_3)_2$, and in the oxidative addition[14] of bis(trimethylsilyl)butadiyne[21] with Cp_2Ti.

The homobimetallic zirconium species[21] $Cp_2Zr(\text{-}C{\equiv}CSiMe_3)Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)Cp_2$ was formed[22] as a byproduct in the reaction mixture of $Cp_2ZrCl_2/BuLi/HC{\equiv}CSiMe_3$, apparently in the reductive elimination[20] of bis(trimethylsilyl)butadiyne from $Cp_2Zr(C{\equiv}CSiMe_3)_2$ and in the oxidative addition[21] of bis(trimethylsilyl)butadiyne with Cp_2Zr.

The spectroscopic and structural data of the mixture prepared according to Scheme 2 display the doubtless existence of the heterobimetallic species $Cp_2Ti(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)Cp_2$ (**4**), in addition to the data of complex **5**.

In the IR spectrum of a single crystal in Nujol suspension, two different absorptions at 1 759 and 1 833 cm^{-1} originate from complex **4**, and one at 1 792 cm^{-1} is assigned to complex **5**. All of them are in the typical region of σ,π-alkinyl-bridged complexes[11].

NMR spectra were measured by dissolving a single crystal just containing a one-to-one mixture of **4** and **5**. The ^1H NMR spectra exhibit two resonances of the Cp (5.05 and 5.38 ppm) and only one resonance for the two equivalent trimethylsilyl groups (0.43 ppm). Also the $^{13}C\{^1H\}$ NMR spectra show two resonances of the Cp (101.2 and 105.5 ppm) and only one resonance for the two equivalent trimethylsilyl groups (2.1 ppm). This indicates a dynamic behaviour of complex **4** in solution at room temperature, as found also for similar complexes[11]. Furthermore, the corresponding signals of the homobimetallic titanium complex **5**, and not those of the homobimetallic zirconium complex, were observed.

In the mass spectra of the mixture of **4** and **5**, molecular ions for the heterobimetallic species (**4**, $M^+ = 592$) and the homobimetallic titanium compound (**5**, $M^+ = 550$), but not from a homobimetallic zirconium complex, were observed.

Crystal data for **4** and **5** were as follows: (obtained from a hexane solution) crystal dimensions: 0.4 × 0.3 × 0.2 mm, prism, red, $a = 11.314(2)$ Å, $b = 14.986(3)$ Å, $c = 16.553(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 96.12(1)°$, space group $P2_1/n$, $Z = 4$, m.w. for $C_{30}H_{38}Si_2Ti_{1.5}Zr_{0.5}$ 572.2, $D_c = 1.362$ g cm^{-3}, number of collected data at 20 °C 8 171, number of unique data 4 292, number of observed data with $I \geq 2\sigma(I)$ 3 338, number of variables 326, R_1 ($I \geq 2\sigma(I)$) 0.0369, wR^2 (all data) 0.1054. Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication.

An X-ray structure analysis differs from the results of the Ti/Ti (ref.[14]) and the Zr/Zr compound[22] and reveals that the single crystal consists of compounds **4** and **5**. Thus the solid state structure (Fig. 1) shows a Zr–Ti disorder and confirms the presence of a heterodinuclear species $Cp_2Ti(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)Zr(\mu\text{-}\eta^1:\eta^2\text{-} C{\equiv}CSiMe_3)Cp_2$.

A Zr–Ti disorder in such complexes is common. The structural data of the disordered complex $Cp_2Ti_{0.75}Zr_{0.25}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)Ti_{0.75}Zr_{0.25}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CSiMe_3)Cp_2$ are very similar to those of the very recent example[11] $Cp_2Ti_{0.5}Zr_{0.5}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CCMe_3)Ti_{0.5}Zr_{0.5}(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CCMe_3)Cp_2$.

From the mechanistic point of view a ring contraction of the zirconacyclocumulene **2** to give a zirconacyclopentadiene complex **3** (Scheme 1) seems possible, in which the free triple bond and one conjugated double bond interact with the titanocene to give the cleavage products. Also a direct external interaction of the cumulene bonding system in **2** with the titanocene instead of the internal interaction in the starting complex as the first step in the reaction seems to be possible.

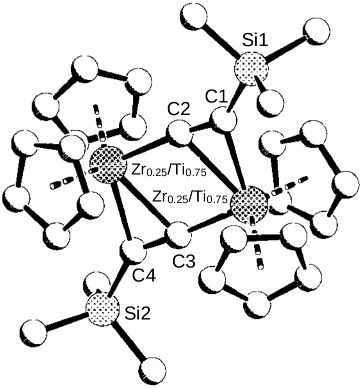


FIG. 1
Solid state structure of one-to-one mixture of **4** and **5**

In conclusion, surprisingly the different types of coupling products of titanocene and zirconocene with bis(trimethylsilyl)butadiyne, the titanacyclopentadiene and the seven-membered zirconacyclocumulene react with sulfur monochloride to give the identical thiophene as the product. In the reaction of the seven-membered zirconacyclocumulene with titanocene, the seven-membered zirconacycle is destroyed, and the resulting butadiyne is cleaved.

Both reactions show, that the titanacyclopentadiene and zirconacyclocumulenes as metallacyclic compounds of different coupling type are not very stable. Especially the seven-membered ring undergoes a stepwise degradation.

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