



Unusual bond activation processes in the reaction of group 4 cyclopentadienyl alkyne complexes with azobenzene

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ABSTRACT

The alkyne complexes $[\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ ($\text{Cp}' =$ substituted or unsubstituted cyclopentadienyl; $\text{M} = \text{Ti, Zr, Hf}$; $\text{L} = \text{Py, THF}$) can serve as metallocene precursors by substitution of the alkyne molecule with other ligands. The reactions of the unsubstituted cyclopentadienyl complexes $[\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**1**) and $[\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**2**) with azobenzene were investigated. In the first case the diazene complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{N}_2\text{Ph}_2)]$ (**3**) was obtained by alkyne exchange. In the reaction of the titanium complex **2** a N=N bond cleavage of azobenzene and a C–H activation of the cyclopentadienyl ligand were observed and the dinuclear imido bridged compound **4** was formed. This mixed valence complex is bridged additionally by a cyclopentadienyl ligand in a $\eta^1:\eta^5$ -coordination mode which is very unusual for titanium complexes. The molecular structures of both compounds were confirmed by X-ray crystallography and compared to former structural data shown in literature.

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1. Introduction

The alkyne complexes of group 4 metals $[\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ ($\text{Cp}' =$ substituted or unsubstituted cyclopentadienyl; $\text{M} = \text{Ti, Zr, Hf}$; $\text{L} = \text{Py, THF}$) can be widely used as metallocene precursors for the synthesis of new compounds [1]. The substitution of the alkyne by different ligands results very often in the formation of metallacycles [2]. Supramolecular structures can be achieved by using ligands with bridging functionalities which are able to link two or more metal centers together [2e,3].

In a former work we described the reaction of different alkyne complexes $[\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ ($\text{M} = \text{Ti}$: $\text{Cp}'_2 = \text{rac-ebthi}$, Cp'_2 , no L; $\text{M} = \text{Zr}$: $\text{Cp}' = \text{Cp}$, $\text{L} = \text{Py}$, $\text{Cp}'_2 = \text{rac-ebthi}$, no L; $\text{rac-ebthi} = \text{rac-1,2-ethylene-1,1'-bis}(\eta^5\text{-tetrahydroindenyl})$) with azobenzene (Scheme 1) [4]. All zirconium complexes as well as $[(\text{rac-ebthi})\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ produced the usual diazametallacycles $[\text{Cp}'_2\text{M}(\text{L})(\text{N}_2\text{Ph}_2)]$. In the case of $[\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ a N=N bond cleavage occurred which yielded besides the formation of the diazametallacycle **I** the two different imido bridged dinuclear complexes **II** and **III**.

We assumed the formation of the two dinuclear complexes by intramolecular C–H activation of the metallocene fragment $[\text{Cp}'_2\text{Ti}]$ to a hydride species. After the coordination of one molecule azobenzene, loss of tetramethylfulvene and cleavage of the N–N bond the imido bridged complexes **II** and **III** are built by coupling of two titanium fragments.

In this work we describe the reactions of the unsubstituted cyclopentadienyl complexes $[\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**1**) and $[\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**2**) with azobenzene.

2. Experimental

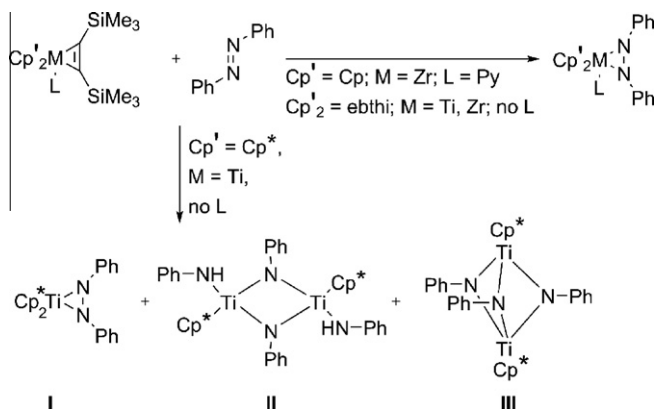
2.1. General

All operations were carried out under argon with standard Schlenk techniques or in a glovebox. Prior to use nonhalogenated solvents (including THF- d_8) were freshly distilled from sodium tetraethylaluminate and stored under argon. $[\text{Cp}_2\text{TiCl}_2]$, $[\text{Cp}_2\text{ZrCl}_2]$ and azobenzene were purchased from Sigma–Aldrich and MCAT (Metallocene Catalysts and Life Science Technologies, Konstanz, Germany) and used without further purification. Complexes **1** and **2** were synthesized according to published procedures [5]. The following spectrometers were used: Mass spectra: MAT 95-XP. NMR spectra: Bruker AV 300. Chemical shifts (^1H , ^{13}C) are given in ppm relative to SiMe_4 and are referenced to signals of the used solvent: THF- d_8 ($\delta_{\text{H}} = 1.73$ and 3.58 , $\delta_{\text{C}} = 25.2$ and 67.4). Melting points: sealed capillaries, Büchi 535 apparatus.

2.2. Preparation of complex 3

Azobenzene (0.091 g, 0.5 mmol) dissolved in THF (5 mL) was added to a solution of complex **1** (0.232 g, 0.5 mmol) in THF (5 mL). The solution was allowed to stand for 24 h at room temperature. The solvent was evaporated under reduced pressure and the crude product dissolved in THF and diethylether. At -78 °C yellow

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Scheme 1. Reactions of different metallocene alkyne complexes with azobenzene.

crystals of complex **3** were formed which were isolated, washed with cold THF and dried in vacuo. Crystals suitable for X-ray analysis were obtained by recrystallization from THF and *n*-hexane at $-78\text{ }^{\circ}\text{C}$ after 1 month. Yield: 0.218 g (0.458 mmol, 92%) $\text{C}_{26}\text{H}_{28}\text{N}_2\text{OZr}$ (475.74 g mol^{-1}). ^1H NMR (300 MHz, 297 K, THF- d_8): δ = 1.78 (m, 4H, THF), 3.63 (m, 4H, THF), 5.96 (s, 10H, Cp), 6.41 (m, 2H, CH_{Ph}), 6.49 (m, 4H, CH_{Ph}), 6.99 (m, 4H, CH_{Ph}). ^{13}C NMR (75 MHz, 297 K, THF- d_8): δ = 26.27 (THF), 68.20 (THF), 112.21 (Cp), 115.51 (CH_{Ph}), 115.60 (CH_{Ph}), 128.56 (CH_{Ph}), 162.45 ($^q\text{C}_{\text{Ph}}$).

2.3. Preparation of complex 4

Azobenzene (0.091 g, 0.5 mmol) dissolved in toluene (5 mL) was added to a solution of complex **2** (0.348 g, 1 mmol) in toluene (5 mL). The solution was stirred for 4 days and cooled down to $-40\text{ }^{\circ}\text{C}$. The resulting reddish brown precipitate was filtrated, washed with cold toluene and dissolved in warm toluene (2 mL). After 2 months at $8\text{ }^{\circ}\text{C}$ brown crystals of complex **4** were formed which were isolated, washed with cold toluene and dried in vacuo. Yield: 0.029 g (0.065 mmol, 13%). Mp: $82\text{ }^{\circ}\text{C}$ (dec.) under Ar. Due to the paramagnetic properties of this complex, no NMR data could be obtained. HR-MS (EI): calc. for $\text{C}_{26}\text{H}_{24}\text{NTi}_2$ 446.08622, found $[\text{M}^+]$ 446.085069. MS m/z (EI): 446 (36) $[\text{M}]^+$, 381 (37) $[\text{M}-\text{Cp}]^+$, 305 (4) $[\text{M}-\text{C}_6\text{H}_5]^+$, 238 (3) $[\text{M}-2\text{Cp}-\text{C}_6\text{H}_6]^+$, 178 (100) $[\text{Cp}_2\text{Ti}]^+$, 113

Table 1
Crystallographic data for complexes **3** and **4**.

	3	4
Chemical formula	$\text{C}_{26}\text{H}_{28}\text{N}_2\text{OZr}$	$\text{C}_{26}\text{H}_{24}\text{NTi}_2$
M (g mol^{-1})	475.72	446.26
Color	yellow	brown
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>
a (\AA)	15.7218(2)	8.3363(4)
b (\AA)	14.9831(3)	17.7805(10)
c (\AA)	18.2968(4)	27.1849(11)
V (\AA^3)	4310.02(14)	4029.4(3)
Z	8	8
Density (g cm^{-3})	1.466	1.471
Crystal size (mm)	$0.50 \times 0.50 \times 0.30$	$0.40 \times 0.35 \times 0.10$
μ (Mo $K\alpha$) (mm^{-1})	0.531	0.805
T (K)	150	200
Number of reflections (measured)	68 614	23 878
Number of reflections (independent)	4943	4289
Number of reflections (observed)	4418	2568
Parameters	271	262
Goodness-of-fit (GOF) on F^2	1.032	0.896
($I > 2\sigma(I)$)	$R_1 = 0.0214$	$R_1 = 0.0476$
All data	$wR_2 = 0.0580$	$wR_2 = 0.0965$

(16) $[\text{CpTi}]^+$. IR (Nujol mull, cm^{-1} , 297 K): ν = 1578 (m), 1260 (m), 1016 (m), 800 (m), 755 (w) cm^{-1} .

2.4. Crystallographic details

Diffraction data were collected on a STOE-IPDS II diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The structures were solved by direct methods (SHELXS-97) [6] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97) [6]. Diamond was used for graphical representations [7]. Crystal data and details of the data collection and the structure refinement of complexes **3** and **4** are given in Table 1.

3. Results and discussion

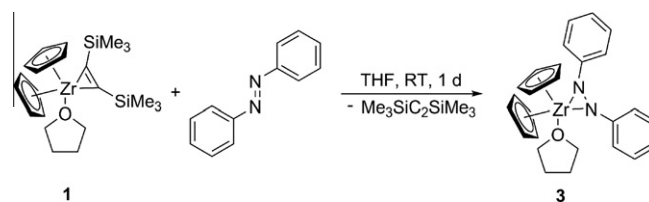
The reaction of $[\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**1**) with azobenzene in THF gives the yellow diazene complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{N}_2\text{Ph}_2)]$ (**3**) (Scheme 2). Commercially available azobenzene exposed to light was used which contains mostly the E but also the Z isomer as well. During the formation of the diazametallacycle an isomerization either before or during the reaction by stepwise coordination to the zirconium center occurred. Complex **3** was previously synthesized by Bergman et al. by reacting $[\text{Cp}_2\text{ZrCl}_2]$ with dilithiumdiphenylhydrazine [8]. They did not succeed in the crystallization of this complex. Only if the THF molecule was exchanged by pyridine the complex $[\text{Cp}_2\text{Zr}(\text{Py})(\text{N}_2\text{Ph}_2)]$ was obtained and its molecular structure characterized by X-ray analysis. Further insertion reactions in the Zr–N bond were performed without isolation.

By recrystallization from THF and *n*-hexane at $-78\text{ }^{\circ}\text{C}$ yellow crystals of complex **3** suitable for X-ray analysis were obtained. The molecular structure is shown in Fig. 1. The diazametallacycle of the zirconocene center is stabilized by an additional THF molecule. Both nitrogen atoms are pyramidal, with a C11–N1–N2–C17 torsional angle of $-95.93(12)^\circ$. The N1–N2 bond length of 1.441(1) \AA falls in the range of other known N–N single bonds [9].

Compared to $[\text{Cp}_2\text{Zr}(\text{Py})(\text{N}_2\text{Ph}_2)]$ the bond lengths of the metallacycle, the bite angle N1–Zr1–N2 and the angles of the coordinated azobenzene molecule C11–N1–N2 and C17–N2–N1 are not significantly different [8]. Only small deviations were found in the bond angles Zr1–N1–C11 and Zr1–N2–C17 probably due to the different sterical demand of the solvent molecule.

In contrast to the two diazametallacycles $[\text{Cp}_2\text{Zr}(\text{THF})(\text{N}_2\text{Ph}_2)]$ and $[\text{Cp}_2\text{Zr}(\text{Py})(\text{N}_2\text{Ph}_2)]$ larger deviations were found between the two corresponding alkyne complexes $[\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ and $[\text{Cp}_2\text{Zr}(\text{Py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ [10]. In the first one the solvent molecule lies in one plane together with the zirconium and alkyne molecule whereas the solvent molecule in the pyridine stabilized complex is out of the plane. Additionally $[\text{Cp}_2\text{Zr}(\text{Py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ shows dynamic NMR spectra due to a free rotation of the alkyne as well as an exchange process of the solvent molecule which was not observed in the corresponding THF stabilized complex. In both cases the diazametallacycles show the same behavior as the pyridine stabilized alkyne complex.

In contrast to the first complex **1** the reaction of two equivalents $[\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ (**2**) with azobenzene gives the paramag-



Scheme 2. Synthesis of the THF stabilized complex **3**.

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