



Insertion of 1-*t*-butylpropyne into singly tucked-in permethyltitanocene. Synthesis, crystal structure of product and transition-state geometry

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ABSTRACT

The singly tucked-in titanocene $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}^{\text{III}}\{\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)\}]$ (**1**) reacted with one equivalent of 1-*tert*-butylpropyne to yield the propenyl-tethered regioisomer $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{C}(t\text{-Bu})=\kappa\text{CMe})]$ (**3**). The exclusive formation of paramagnetic **3** was proved experimentally and steric reasons were clarified by DFT calculation of transition state which involves both π -systems on the alkyne for bonding interaction with the metal and with sp^2 carbon atom of exomethylene group of **1**. The obtained compound **3** is by 40 kJ/mol lower in energy than its hypothetical isomer having *t*-Bu group on C_α of the tether.

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1. Introduction

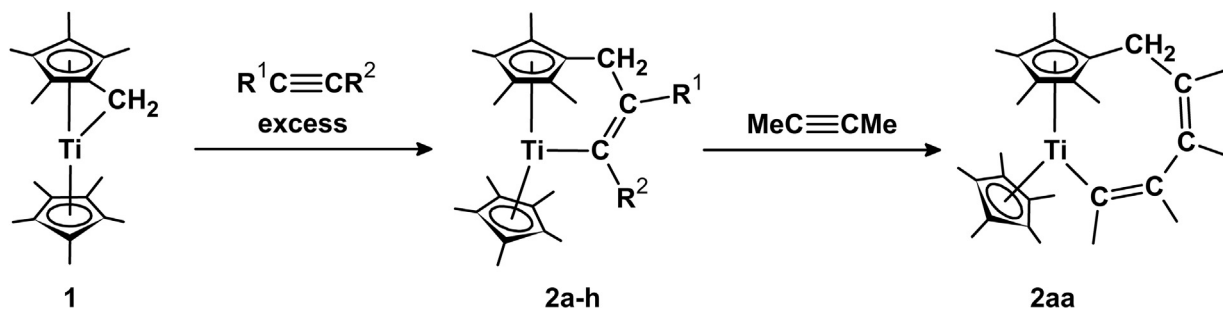
The singly tucked-in permethyltitanocene (**1**) was shown to react with internal alkynes to offer a series of propenyl-tethered titanocene (Ti^{III}) derivatives (**2a–h**) (Scheme 1). Only in the case of 2-butyne was the parent 1:1 adduct **2a** capable of inserting another molecule of the same alkyne, which yielded the pentadienyl-tethered compound **2aa**. All other alkynes carrying more bulky substituents (including $\text{R}^1, \text{R}^2 = \text{Et}$) were reluctant towards inserting a second alkyne molecule. Investigating alkynes having disparate substituents, the mode of insertion was found to be driven by the polarity of the $\text{Ti}^{(\delta+)}\text{-C}_\alpha^{(\delta-)}\text{R}^1=\text{C}_\beta$ bond. The electron-attracting groups (Ph, alkynyl, SiMe_3) resided preferably on the α -carbon, whereas the electron donating alkyl groups (Me, *t*-Bu) preferred the more positive β -carbon of the propenyl tether. Nonetheless, steric demands were also playing important role during the insertion, as exemplified by the reluctance of **1** to react

with sterically hindered alkynes – bis(trimethylsilyl)ethyne, 1-*tert*-butyl-2-(trimethylsilyl)ethyne or 2,4-di-*tert*-butyl-but-1-ene-3-yne [1]. The transition-state molecules of the insertion step were studied by Density Functional Theory (DFT) for symmetrical 2-butyne and 3-hexyne which were held in the bent titanocene equatorial plane. Importance of steric demands became evident from the above mentioned reluctance to insert the second molecule of 3-hexyne.¹

In this paper we report on obtaining of the yet unknown propenyl-tethered titanocene $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{C}(t\text{-Bu})=\kappa\text{CMe})]$ (**3**) from **1** and 1-*tert*-butylpropyne (4,4-dimethyl-2-pentyne), whose both substituents feature very similar electron donating properties, thus the mode of alkyne addition is expected to be controlled sterically. The reaction intermediate leading to formation of **3** bearing the bulkier *t*-butyl group on the β -carbon of the propenyl tether is clarified by determining the transition-state geometry using Density Functional Theory.

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	R ¹	R ²
2a*	Me	Me
2b	Et	Et
2c	Ph	Ph
2d	Me	Ph
2e	Me	SiMe ₃
2f	CMe ₃	C≡CCMe ₃
2g	SiMe ₃	C≡CSiMe ₃
2h	Ph	SiMe ₃
2h'	SiMe ₃	Ph

* 1: MeC≡CMe = 1:1

Scheme 1.

2. Materials and methods

2.1. General comments and methods

The reaction of **1** with 1-tert-butylpropyne for obtaining **3** was performed in all-sealed glass vacuum systems using magnetically breakable seals. Using the same technique, compound **3** was chlorinated with PbCl₂ or reacted with hydrogen at atmospheric pressure, and the products of the latter reaction were chlorinated with PbCl₂. Crystalline samples for EI-MS measurements and melting point determinations were placed into glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Samples in sealed capillaries were opened and inserted into the direct inlet under argon. The mass spectra are represented by the peaks of relative abundance higher than 10% and by important peaks of lower intensity. ¹H (299.98 MHz) and ¹³C (75.44 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 298 K. Chemical shifts (δ/ppm) are given relative to the solvent signal (C₇D₈: δ_H 7.15, δ_C 128.00). EPR spectra were recorded on a MiniScope MS400 (Magnettech GmbH, Berlin, Germany) equipped with a microwave frequency counter FC 400 and a temperature controller H03. UV–vis spectra in the range 300–800 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma) and were digitized using an in-house made A/D conversion unit and collection software. Samples in KBr pellets were prepared and pressed in a glovebox Labmaster 130 (mBraun) and their IR spectra were recorded in an air-protected pellet holder on a Nicolet Avatar FT IR spectrometer in the range of 400–4000 cm⁻¹.

2.2. Chemicals

Solvents hexane, toluene, and tetrahydrofuran (THF) were dried by refluxing over LiAlH₄ and stored as solutions of green dimeric titanocene [(μ-η⁵:η⁵-C₁₀H₈)(μ-H)₂{Ti(η⁵-C₅H₅)₂}]₂ [ref. [2]] on a vacuum line. Toluene-*d*₈ (C₇D₈) (Sigma Aldrich) was degassed, distilled under vacuum on singly tucked-in permethyltitanocene [Ti(C₅Me₅)(C₅Me₄CH₂)] (**1**) [3], and stored as its solution on a vacuum line. Compound **1** was prepared by thermolysis of [(C₅Me₅)₂TiMe] in toluene at 110 °C for 3 h.¹ 4,4-Dimethyl-2-pentyne (MeCCt-Bu) (97%, Alfa Aesar) (5.0 mL) was degassed, distilled onto **1** (~0.05 g), and stored on a vacuum line equipped with metal valves.

2.2.1. Preparation of [(η⁵-C₅Me₅)Ti(η⁵:η¹-C₅Me₄CH₂C(*t*-Bu)=κCMe)] (**3**)

A solution of **1** (0.2 M, 5.0 mL, 1.0 mmol) in hexane was added to an excess of 1-tert-butylpropyne (0.3 mL, 2.2 mmol) distilled into a three-necked ampule on a vacuum line. The initial purple solution turned yellowish brown after standing overnight. After warming to 60 °C for 1 h all volatiles were distilled off under vacuum and a brown solid was dissolved in 3 mL of hexane. A slow distillation of hexane into one ampule arm placed close to a cooling wall of refrigerator afforded brownish-yellow crystals in brown mother liquor (~0.2 mL). The mother liquor was poured to the distillate, the crystalline solid was dissolved in minimum hexane and the crystallization was twice repeated. The resulting brownish-green crystals were dried in vacuum and sealed off in the other ampule arm. This sample was opened in glovebox, weighed and suitable crystals were transferred into capillaries for X-ray diffraction measurements. Yield 0.19 g (46%).

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