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Journal of Organometallic Chemistry 580 (1999) 210–213

Journal of Organo metallic Chemistry

A directly ring-to-ring linked ferrocene–pseudotitanocene complex

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Received 1 October 1998

Abstract

Addition of excess ferrocenylacetylene (FcC≡CH) to $[\eta^5\text{-}(C_5H_5)Ti][\mu\text{:}\eta^2\text{:}\eta^2\text{-}C_2(SiMe_3)_2]_2[\eta^5\text{-}(C_5H_5)Mg]$ (**1**) affords the novel ferrocene–pseudotitanocene complex $[\eta^5$-1,2,5,6-tetrakis(trimethylsilyl)-4-ferrocenylcyclohexa-1,4-dienyl](η^5-cyclopentadienyl)-titanium(II), $[\eta^5\text{-}(Me_3Si)_4FcC_6H_2]Ti(\eta^5\text{-}C_5H_5)$ (**2**), as the sole isolated titanium-containing product. Its structure was established by EI MS, NMR and UV–vis spectroscopy. The formation of **2** follows the general reaction route of terminal acetylenes with **1**.

Keywords: Titanium(II); Ferrocene–pseudotitanocene complex; Ferrocenylacetylene; Cyclopentadienyl–cyclohexadienyl bond; NMR spectra

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1. Introduction

Looking for synthetic methods leading to organometallic compounds containing two or more metal atoms linked by a hydrocarbon chain, two main methods become obvious. Firstly, the direct use of a functionalized organometallic compound as the ligand in transition metal complexes and secondly, a synthetic transformation of an organometallic compound (its substituents) into a new compound. In the case of ferrocene derivatives, the first route may be documented by many syntheses and applications of complexes with ferrocene-based ligand such as phosphines, mixed *P*,*N*-donors etc. reported in the literature [1]. As for the application of the second approach in the chemistry of ferrocenes, ethynylferrocene [2] is a frequently used, extremely versatile starting compound. One straightforward method for transformation of its triple bond into a linking group is the simple deprotonation of ethynylferrocene yielding σ-complexes of the M–C≡CFc (Fc = ferrocenyl) type [3]. The formation of carbenes M=C(R)CH$_2$Fc (M = Ru [4]) or vinylidene complexes M=C=CFc(R) (M = Rh [5]) might serve as another example. Application of derivatives containing a spacer between ferrocenyl and ethynyl groups further increases the scope of accessible complexes [6,7]. In spite of a variety of synthetic tools, however, the combinations of early and late transitions metals are rather rare [8]. For titanium, the following titanocene bis(acetylide) complexes have been reported so far: $(\eta^5\text{-}C_5H_4(SiMe_3)]_2Ti(\eta^1\text{-}C{\equiv}CFc)_2$, its tweezer complex with an embedded Ni(CO) group [9] and $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C{\equiv}CC{\equiv}CFc)_2$ [10]. We have used ethynylferrocene to mimic the reaction of terminal acetylenes with the titanium–magnesium complex $[\eta^5\text{-}(C_5H_5)\text{-}Ti][\mu\text{:}\eta^2\text{:}\eta^2\text{-}C_2(SiMe_3)_2]_2[\eta^5\text{-}(C_5H_5)Mg]$ (**1**) [11]. In this reaction a terminal acetylene takes part in the formation of a tetrakis(trimethylsilyl)-substituted cyclohexadienyl ligand affording the corresponding (η^5-cyclohexadienyl)(η^5-cyclopentadienyl)titanium(II) complex (Scheme 1) [12].

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PII: S0022-328X(98)01147-4

2. Experimental

2.1. General data and methods

All manipulations and spectroscopic measurements were performed under high-vacuum conditions using all-sealed glass devices equipped with breakable seals. UV–vis spectra in the range of 280–2000 nm were obtained on a Varian Cary 17D spectrometer in all-sealed quartz cuvettes (Hellma). NMR spectra were recorded in C_6D_6 solutions on a Varian UNITY Inova 400 spectrometer (^{1}H 399.95 MHz, ^{13}C 100.58 MHz) at 21°C. ^{29}Si-NMR spectra (79.46 MHz) were measured by a standard DEPT pulse sequence. The chemical shifts (δ/ppm) were referenced to the solvent signal (δ_H 7.15, δ_C 128.0) or to external TMS (δ_{Si} 0). The assignment of the ^{1}H- and ^{13}C-NMR signals was based on ^{1}H-, ^{13}C{^{1}H}-, ^{13}C APT and ^{1}H-, ^{1}H-COSY spectra. Crystals for EI MS measurements and melting point determinations were placed into glass capillaries and KBr pellets for IR spectra were prepared in a glovebox Labmaster 130 (mBraun) under purified dinitrogen. Mass spectra were measured on a VG 7070E instrument (direct inlet, EI, 70 eV; only important mass peaks and peaks of relative abundance higher than 7% are reported). IR spectra were measured on a Specord 75 IR (Zeiss, Jena, Germany) spectrometer using an air-protecting cell. The melting point was determined in sealed glass capillaries under dinitrogen, and is uncorrected. Semiempirical calculations on **2** and **3** were performed using a ZINDO method [13]. The coordinates obtained were transferred into a PLUTO program for drawing.

2.2. Chemicals

The solvents hexane, and toluene were purified by conventional methods, dried by refluxing over $LiAlH_4$, and stored as solutions of dimeric titanocene $(C_{10}H_8)[(C_5H_5)Ti(\mu\text{-}H)]_2$ [14]. The complex FcC≡CH was synthesized from acetylferrocene using the literature procedure ([2]d). The complex $[(\eta^5\text{-}C_5H_5)Ti][\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(SiMe_3)_2]_2[(\eta^5\text{-}C_5H_5)Mg]$ (**1**) was prepared by the reduction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ by excess magnesium metal in THF in the presence of bis(trimethylsilyl)acetylene [11].

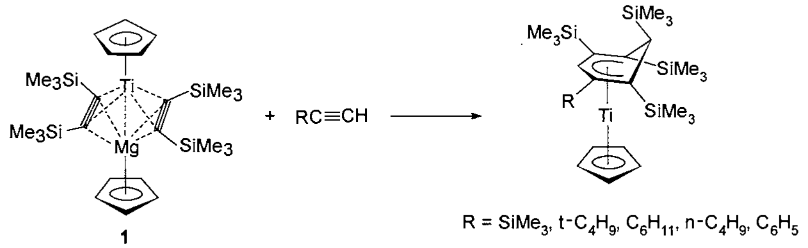
2.3. Preparation of $[\{\eta^5\text{-}C_6H_2Fc(SiMe_3)_4\}Ti(\eta^5\text{-}C_5H_5)]$ (2)

A toluene solution of FcC≡CH (3.16 g, 15 mmol in 45 ml) was added to solid **1** (1.6 g, 3 mmol). The orange reaction mixture turned immediately dark red–brown. After warming to 60°C for 20 min, all volatiles were evaporated in vacuo at 60°C and the residue was extracted with hexane. The hexane fraction was evaporated and slowly extracted by condensing hexane vapor. The brown, readily soluble fraction was separated and after evaporation of hexane analyzed by mass spectrometry. The residue was partly dissolved in warm hexane to give a brown green solution. Brown solid residues which adhered to the glass walls were discarded. This evaporation/dissolution procedure was repeated twice to afford a khaki green solution. Concentration and slow cooling of the solution gave dark green crystals of **2**. Yield 0.45 g (23% vs. **1**); m.p. 314°C. ^{1}H-NMR (C_6D_6): −0.14, −0.01, 0.32, 0.41 (s, 9 H each; *Me*$_3$Si), 0.40 (s, 1 H, sp^3-C*H*), 2.79 (ddd, 1H, A of ABCD C_5H_4, $J_{AB} = 2.5$ Hz, $J_{AC} = 1.3$ Hz, $J_{AD} = 1.3$ Hz), 3.82 (ddd, 1H, B of ABCD C_5H_4, $J_{BC} = 2.4$ Hz, $J_{BD} = 1.3$ Hz), 3.92 (ddd, 1 H, C of ABCD C_5H_4, $J_{CD} = 2.4$ Hz), 4.23 (s, 5 H, C_5H_5Fe), 4.70 (ddd, 1 H, D of ABCD C_5H_4), 5.86 (s, 1 H, sp^2-C*H*), 6.07 (s, 5 H, C_5H_5Ti); ^{13}C{^{1}H}-NMR (C_6D_6, all signals singlets): 2.1, 2.7, 2.9, 3.3 (*Me*$_3$Si), 25.8 (sp^3-*C*H), 66.0, 67.3, 69.3, 70.6 (*C*H of C_5H_4), 70.0 (C_5H_5Fe), 94.8 (C_{ipso} C_5H_4), 110.6 (C_5H_5Ti), 113.6, 117.2, 122.3, 130.6 (sp^2-C_{quatt}), 114.5 (sp^2-*C*H); ^{29}Si-NMR (C_6D_6): −12.4, −12.2, −2.1, 9.8 (4 non-equivalent *Si*Me$_3$ groups); IR (KBr, cm^{-1}): 3080 (b,m), 2942 (s), 2885 (m), 1592 (vw), 1473 (vw), 1407 (w), 1344 (w), 1313 (vw), 1256 (sh), 1240 (vs), 1147 (w), 1100 (s), 1055 (w), 1020 (sh), 1007 (m), 998 (m), 956 (m), 918 (vw), 874 (m), 830 (vs), 787 (s), 773 (s), 746 (s), 675 (m), 633 (b,m), 582 (vw), 532 (w), 507 (m), 487 (w), 456 (w), 446 (vw); UV–vis (hexane): 335 > 420sh > > 585 > 880 nm; EI MS (direct inlet, 70 eV, 200°C): *m*/*z* (%)) 664 ($M^{+\bullet}$, 9), 594 (10), 593 (28), 592 (54), 591 ($[M{-}SiMe_3]^+$, 100), 590 (46), 589 (51), 588 (17), 587 (19), 478 (10), 468 (8), 467 (12), 454 (9), 180 (7), 179 (14), 178 ($[(C_5H_5)_2Ti]^+$, 76), 177 (9), 176 (10), 113 (12), 73 (73), 45 (12). The elemental composition of $M^{+\bullet}$ ($M = C_{33}H_{52}Si_4FeTi$) has been confirmed by a comparison of its simulated and experimental isotopic patterns. No attempt to obtain elemental analysis was made because of high sensitivity of **2** towards water and oxygen.

After evaporation of the highly soluble fraction, the rusty brown residue was analyzed by EI MS. The temperature of the probe was increased slowly while the spectra were acquired. The following components were identified on the basis of their molecular ions: *m*/*z* 210 (FcC≡CH), 212 (FcCH=CH$_2$), 282 (FcC≡CSiMe$_3$), 284 (FcCH=CHSiMe$_3$), 382 (not assigned), 420 ([FcC≡CH]$_2$), 478 ($C_6H_2Fc(SiMe_3)_3$), 518 ($C_6H_3Fc_2(SiMe_3)$), 590 ($C_6H_2Fc_2(SiMe_3)_2$) and 630 ($C_6H_3Fc_3$).

3. Results and discussion

Addition of an excess of FcC≡CH (five equivalents) to **1** in toluene gave a mixture of compounds containing



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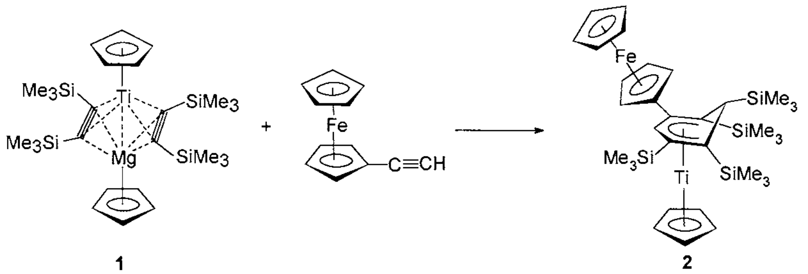
Scheme 1.



1 2

Scheme 2.

(η^5-1,2,5,6-tetrakis(trimethylsilyl)-4-ferrocenylcyclohexa-1,4-dienyl)(η^5-cyclopentadienyl)titanium(II), [η^5-$(Me_3Si)_4FcC_6H_2$]Ti(η^5-C_5H_5) (**2**) as the main titanium-containing product (Scheme 2).

Fractional crystallization and extraction yielded pure **2** as a khaki green crystalline material composed of aggregates of very thin needles. All attempts to grow X-ray quality crystals were unsuccessful. Generally, the reaction follows in most respects the pathway outlined in Ref. [12] including the formation of byproducts. An MS analysis of the more soluble fraction of products demonstrated the presence of unreacted FcC≡CH, and partially reduced, silylated and/or oligomerized ferrocene derivatives $FcCH{=}CH_2$, $FcC{\equiv}CSiMe_3$, $FcCH{=}CHSiMe_3$, $[FcC\equiv CH]_2$, and cyclotrimers $C_6H_{6-x-z}Fc_x(SiMe_3)_z$,($x/z$ = 1/3, 2/1, 2/2, 3/0).

^1H- and ^{13}C-NMR spectra of **2** are in full agreement with the data reported previously for the analogous mononuclear titanium complexes bearing other substituents (trimethylsilyl, cyclohexyl, phenyl, or *tert*- and *n*-butyl) [12] instead of ferrocenyl. The presence of the pentasubstituted cyclohexadienyl ligand was confirmed by the NMR signals at δ_H 5.86, δ_C 114.5 and δ_H 0.40, δ_C 25.8 for sp^2-CH and sp^3-CH, respectively. As the result of the direct connection of the ferrocenyl Cp-ring to the chiral η^5-cyclohexadienyl ligand, the proton signals of the substituted Cp-ring fall into four well-resolved multiplets of the ABCD spin system although these are usually observed as a pair of apparent triplets of a highly degenerate AA′BB′ spin system. The *J*-values obtained by numerical simulation correspond well to the values typical for tri- and tetrasubstituted ferrocenes [15]. The signals of ferrocenyl CH groups were found within the δ_C range of 66–70 whereas the C_{ipso} signal is markedly downfield-shifted (δ_C 94.8). The orientation of the $SiMe_3$ group attached to the sp^3 carbon atom of the cyclohexadienyl ligand could not be determined from the NMR spectra. A structure optimalization of **2** by ZINDO calculations [13] revealed that the $SiMe_3$ group at the sp^3 carbon atom is located in *endo*-position (Fig. 1). A similar calculation for [η^5-1,2,4,5,6-pentakis(trimethylsilyl)cyclohexadienyl](η^5-cyclopentadienyl)titanium(II) **3** showed the *exo*-attachment of the $SiMe_3$ group. This is in agreement with the crystal structure of **3** [12]. Although the calculated bond lengths of Ti–C and Fe–C differ considerably from the crystal structure data for **3** and, e.g. 1,3,5-tris(ferrocenyl)benzene [16], the calculated *endo*-position seems to reflect the mutual crowding of the Fc ligand and the $SiMe_3$ groups.

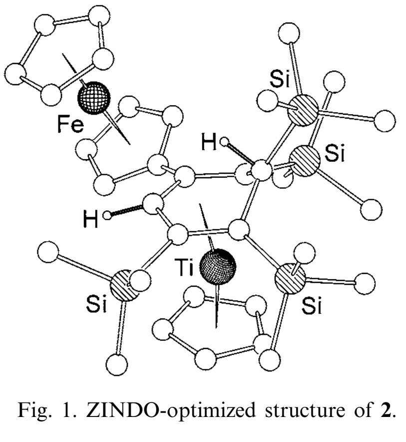


Fig. 1. ZINDO-optimized structure of **2**.

The mass spectra clearly show the molecular peak m/z 664 ($\mathbf{2}^{+\cdot}$) and peaks m/z 591, 178, 73, corresponding to $[M-SiMe_3]^+$, $[\{C_5H_5)_2Ti]^+$ and the $[SiMe_3]^+$ fragment ions, respectively. The loss of the trimethylsilyl group indicates the stabilization of ionized species through the formation of a tetrasubstituted benzene ligand. A similar fragmentation feature was observed for the organic analogues mentioned above. Compared to their fragmentation patterns, however, the fragmentation of **2** is rather simple. The second most populated fragmentation process is the transfer of the cyclopentadienyl ligand from iron to titanium leading to the formation of the $[(C_5H_5)_2Ti]^+$ ions.

The electronic absorption spectrum of **2** displays absorption bands at 580 and 880 nm, i.e. within and close to the regions where absorption bands for the analogous pseudotitanocene complexes are observed. Interestingly, the band at 880 nm is at the longest wavelength among other pseudotitanocene congeners. Whether it is related to a strong electron releasing effect of the Fc group is not certain as the order of substituents from the shortest wavelength is as follows: $SiMe_3$ 813, *tert*-butyl 840, *n*-butyl 860, phenyl 860, and cyclohexyl 865 nm [12].

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/96/0948).

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