Novel *trans*-η^2-Alkyne Complexes of Titanocene with Strong Si−H−Ti Interactions. Synthesis, Spectral Characteristics, and X-ray Crystal Structure

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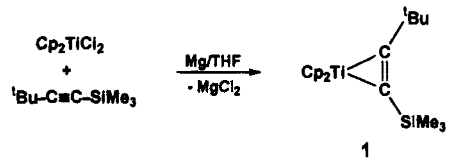
Group 4 bent metallocene complexes are interesting organometallic building blocks,[1] especially in organosilicon chemistry.[2] Among them, stable alkyne complexes, e.g., $Cp^*_2Ti(\eta^2$-acetylene) or $Cp_2Ti(\eta^2$-acetylene), are very rare.[3] Recently we obtained such silylalkyne complexes, e.g., $Cp_2Ti(\eta^2\text{-}PhC_2SiMe_3)$,[4] and also complexes with bis(trimethylsilyl)acetylene, e.g., $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[4] and $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = thf,[5a] py[5b]), being excellent generators for "Cp_2M" under mild conditions in reactions with alkynes,[4] butadiynes,[6a,b] or acetylenedicarboxylates.[6c]

Here we report about the interaction of titanocene and alkynylsilanes yielding different types of complexes. In the case of $^tBuC{\equiv}CSiMe_3$ the complex free from further ligands $Cp_2Ti(\eta^2\text{-}{}^tBuC_2SiMe_3)$ with alkyne substituents in a *cis* position was obtained. Alkynylsilanes, carrying Si−H groups like $RC{\equiv}CSiMe_2H$ (R = ^{t}Bu, Ph, $SiMe_2H$), yield $Cp_2Ti(\eta^2\text{-}RC_2SiMe_2H)$ complexes with a *trans* arrangement of the alkyne substituents, in which the Si and H atoms interact with Ti. These transition metal *trans*-η^2-alkyne complexes show a temperature-dependent behavior with strong Si−H−Ti interactions at low temperature.

Well-known is the reduction of titanocene dichloride with magnesium, which gives with $^tBuC{\equiv}CSiMe_3$ in THF at room temperature (eq 1) complex $Cp_2Ti(\eta^2\text{-}{}^tBuC_2SiMe_3)$ (**1**).[7]

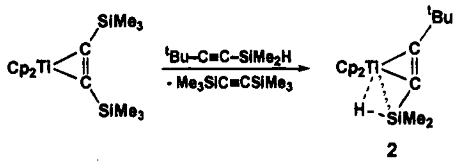


(1)

1

The absorption at 1686 cm^{-1} in the IR spectrum and the signals of the acetylenic C atoms at 205.4 (*C*SiMe$_3$) and 236.5 (*C*^{t}Bu) ppm in the ^{13}C NMR spectrum are typical for analogous alkyne complexes[4] and indicate a titanacyclopropene structure for complex **1**. The crystal structure of **1**[8] exhibits an unsymmetric *cis* conformation of the complexed alkyne [Ti−C(Si), 2.103(3) Å; Ti−C(^{t}Bu), 2.018(3) Å; Si−C1−C2, 148.9(3)°; C1−C2−C3, 138.6(3)°]. The distance of the coordinated C≡C triple bond (C1−C2 1.280(5) Å) is close to the value of a C=C double bond (1.28−1.31 Å[9]).

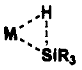
The reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[4b] with $^tBuC{\equiv}CSiMe_2H$ in *n*-hexane leads to an alkyne substitution. After crystallization at −78 °C, air- and moisture-sensitive dark red crystals of **2**[10] were obtained in 46% yield. The titanocene complex is stable in solution at room temperature and shows a temperature-dependent Si−H−Ti interaction in **2** (eq 2).



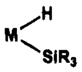
(2)

2

The IR spectrum and the temperature-dependent ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **2** (Table 1) give strong evidence for a Si−H−Ti interaction, studied in detail and normally described by the different structures **A** and **B**.[2a,11,12]



A



B

Some group 4 metallocene complexes having such structures have been described already.[12] A related agostic β-Si−H interaction in silylamido complexes of zirconocene has been studied in detail.[12c]

At 303 K the ^{1}H NMR spectrum of **2** exhibits a broad resonance at −3.74 ppm (Ti−H) and a broad doublet at −0.02 ppm ($^3J_{HH}$ 2.5 Hz, SiMe$_2$) in addition to the ^{t}Bu and Cp signals. The ^{29}Si NMR spectrum shows a doublet at −0.5 ppm ($^1J_{Si,H}$ 123 Hz). In the ^{13}C NMR spectrum of **2** only one signal of a metal-coordinated C atom at 216.2 ppm (*C*^{t}Bu) is observed in the expected downfield region, e.g., **1**: 236.5 ppm (*C*^{t}Bu). The other signal at 116.4 ppm (*C*SiMe$_2$H) occurs upfield, e.g., **1**: 205.4 ppm (*C*SiMe$_3$). The obtained room temperature NMR parameters are typical for complexes with Si−H−Ti interaction of type **A**.[12]

At 193 K in the ^{1}H NMR spectrum the hydrogen signal is dramatically shifted from 4.46 ppm for the free alkyne to −7.32 ppm in **2**. The signal of the Si−Me groups becomes a singlet at 0.07 ppm without coupling to the hydrogen (e.g., uncoordinated SiMe$_2$H: doublet, $^3J_{HH}$ 3.7 Hz). From the ^{29}Si NMR spectrum comes the strongest evidence for a Si−H−Ti interaction with a coupling constant J_{SiH} of 93 Hz, 106 Hz less than

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(8) Crystal data for **1**: *a* = 15.833(4) Å, *b* = 8.789(2) Å, *c* = 14.959(4) Å, space group $P2_1/c$, $Z = 4$, mol wt = 332.4 for $C_{19}H_{28}SiTi$, δ(calcd) = 1.15 g/cm^3, $R = 0.064$, $R_w = 0.83$. Full details will be published in ref 7.

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(10) **2**: IR (Nujol) 1685, 1747 cm^{-1} (free alkyne: 2157, 2139 cm^{-1}); ^{1}H NMR (toluene-d_8, 303 K) δ −3.74 (m, 1H), −0.02 (d, $^3J_{HH}$ = 2.5 Hz, 6H), 1.05 (s, 9H), 5.28 (s, 10H); ^{13}C NMR (toluene-d_8, 303 K) δ −2.5 ($^1J_{SiC}$ = 61 Hz), 32.6, 40.6, 105.8, 116.4 (*C*SiMe$_2$) 216.2 (*C*^{t}Bu); ^{29}Si NMR (toluene-d_8, 303 K) δ −0.5 (J_{SiH} = 123 Hz).

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Table 1. Selected NMR Data for **2** and the Parent Alkyne

		^{t}BuC≡CSiMe$_2$H	**2** at 303 K	**2** at 193 K
^{1}H NMR	δ Si*H*	4.46	−3.74	−7.32
	δ Si*Me*$_2$	0.18	−0.02	0.07
	$^3J_{H,H}$	3.7	2.5	
^{13}C NMR	δ *C*(Si)	79.6	116.4	89.4
	δ *C*(^{t}Bu)	117.5	216.2	206.1
^{29}Si NMR	δ *Si*	−38.6	−0.5	17.6
	$^1J_{Si,H}$	199	123	93

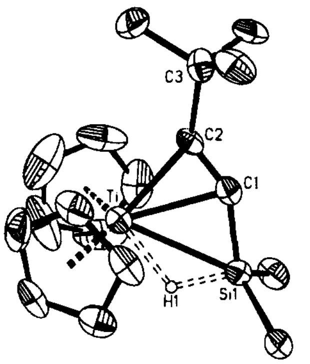


Figure 1. Structure of **2**. Selected bond distances (Å) and angles (deg): C1−C2, 1.275(9); Ti−C1, 2.276(7); Ti−C2, 2.162(7); Si−C1, 1.766(7); Ti−Si, 2.655(2); Ti−H1, 1.82(5); Si−H1, 1.42(6); Ti−H1−Si, 109(1); H1−Si−C1, 98(2); Si−C1−C2, 149.5(6); C1−C2−C3, 135.2(7); C1−C2−Ti, 78.3(4); C2−Ti−H1, 105(2).

in the free alkyne (199 Hz). The δ (*Si*Me$_2$) value of 17.6 ppm is 56.2 ppm downfield shifted from the parent alkynylsilane (δ −38.6 ppm). The ^{13}C NMR chemical shifts at 193 K for *C*^{t}Bu (δ 206.1) and *C*SiMe$_2$H (δ 89.4) carbon atoms are noticeably upfield compared to the shifts for the same atoms at 303 K.

The solid state structure of **2**[13] is shown in Figure 1. The exchange of one Me group in **1** by a H atom in **2** gives the bend of the Si group in the opposite direction, to a *trans* conformation of the complexed alkyne in **2** in contrast to the *cis* conformation in **1**. The H atom could be found and refined smoothly despite the neighborhood of strong scattering elements and is unsymmetrically bonded between Ti and Si. The Ti−H bond of 1.82(5) Å is in the normal range (1.66−1.97 Å) for titanium hydride complexes,[12b] and the Si−H distance of 1.42(6) Å is in accordance with the typical region of tetrahedral silanes [1.48(2) Å[11a]]. The Ti−Si distance of 2.655(2) Å is in the region of titanocene silyl derivatives (2.60−2.67 Å[2b]). The C1−Si1 bond distance of 1.766(7) Å is between a C−Si single bond (1.87−1.91 Å[9]) and the C=Si double bond length in West's first stable 1-silaallene [1.704(4) Å],[14] near to the region of η^2-silene complexes (1.78−1.80 Å).[15] It is somewhat shorter than in a ruthenium 1-silaallene complex [1.805(6) Å], very recently published by Jones.[16]

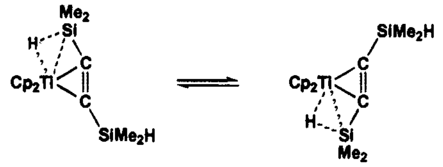
The sum of bond angles around Si in **2** of 342.6° is similar to that in η^2-silene complexes [cf. 343° in Cp*(iPr$_3$P)Ru(H)(η^2-H$_2$C=SiPh$_2$),[15a] 341° in Cp*(Me$_3$P)Ir(η^2-H$_2$C=SiMe$_2$),[15b] and 348° in Cp$_2$W(η^2-H$_2$C=SiMe$_2$)[15c]] and the new silaallene complex [cf. 345.5° in Cp*(Cy$_3$P)Ru(Ph$_2$CCSiMe$_2$H)[16]], corresponding to a hybridization of the silicon between sp^2 (360°) and sp^3 (329°). The Ti−C1 bond length in **2** (2.276(7) Å) is larger compared to that in **1** [2.103(3) Å]. The C1−C2 distance of 1.275(9) Å in **2** is close to a value of a C=C double bond.

Some features of **2**, e.g., the short Si1−H distance of 1.42(6) Å and the relatively high coupling constant J_{SiH} of 93 Hz at 193 K, may be explained by a "frozen intermediate" in the oxidative addition of the Si−H bond to the metal, respectively an incomplete hydrogen transfer, found in the 1-silaallene complex Cp*(Cy$_3$P)Ru(Ph$_2$CCSiMe$_2$H) [J_{SiH} 66 Hz, Si1−H distance 1.70(3) Å[16]] in contrast to the complete transfer in the η^2-silene complex Cp*(iPr$_3$P)Ru(H)(η^2-H$_2$C=SiPh$_2$) (20 Hz).[15a]

The results of NMR measurements at 193 K [extremely high field shift δ (H) −7.32 ppm; δ (*Si*Me$_2$) 17.6 ppm, specific for sp^2-Si; Me−Si groups as singlet, δ (*C*SiMe$_2$) 89.4 ppm] and X-ray structural data [*trans* arrangement of the alkyne substituents; short C1−Si distance; normal Ti−Si and Ti−H bond lengths; sum of angles (342.6°) around Si] are in agreement with a description of **2** on the way to a hydride η^3-silaallenyl complex, analogous to Wojcicki's η^3-phenylallenyl zirconocene complexes.[17]

In summary, judged by the high J_{SiH} coupling constant of 93 Hz the transfer of H to Ti is not complete and the Si−H bond appears not to be fully broken.[12c,15b]

The complexes Cp$_2$Ti(HMe$_2$SiC$_2$SiMe$_2$H) (**3**) and Cp$_2$Ti(PhC$_2$SiMe$_2$H) were obtained in the reaction of other alkynylsilanes as HMe$_2$SiC≡CSiMe$_2$H or PhC≡CSiMe$_2$H instead of ^{t}BuC≡CSiMe$_2$H with Cp$_2$Ti(Me$_3$SiC$_2$SiMe$_3$). They also show the Si−H−Ti interaction.[18] Complex **3** carrying two Si−H functions exhibits an additional dynamical behavior in a "flip-flop" coordination:[19]



The alternating coordination of both SiH subunits is indistinguishable on the NMR time scale at 303 K, but at 165 K NMR spectra display different signals of the free and the interacting halves of the alkyne [^{1}H NMR, δ 4.58 and −8.04; ^{13}C NMR, δ (C≡C) 182.3 and 119.8; ^{29}Si NMR, δ −22.7 ($^1J_{SiH}$ 176 Hz) and 34.3 (J_{SiH} 92 Hz)]. The data of the complexed SiH group in **3** are very near to those of complex **2**.

Attempts to prepare a titanium-stabilized silylium cation or cationic complexes by hydrogen abstraction from **2** or **3** are in progress.

Compound **2** shows a new type of complexation and represents the first example of a transition metal *trans*-η^2-alkyne complex with temperature-dependent Si−H−Ti interaction.

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Supporting Information Available: Tables of crystal structure and details of data collection, bond angles and distances, and atomic positional and thermal parameters of **2** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[13] Crystal data for **2** (suitable crystals from a THF/*n*-hexane mixture including one uncoordinated THF molecule, stable in the solid up to 0 °C): $a = 8.730(1)$ Å, $b = 15.195(2)$ Å, $c = 16.704(2)$ Å, $\beta = 103.92(1)°$, $V = 2150.8(5)$ Å^3, space group $P2_1/a$, $Z = 4$, mol wt = 390.48 for C$_{22}$H$_{34}$OSiTi, δ(calcd) = 1.206 g/cm^3, $\lambda = 0.710\,69$ Å, measured reflections 3253, independent reflections 3133, observed reflections 1653, refined parameters 205, $R = 0.073$ and w$R_2 = 0.178$.

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[18] **3**: IR (Nujol) 1771, 1759, 2106 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 303 K) δ −0.96 (br, 2H), 0.27 (d, $^3J_{HH}$ = 2.9 Hz, 12H), 5.03 (s, 10H); ^{13}C NMR (C$_6$D$_6$, 303 K) δ −2.2, 103.0, 162.3; ^{29}Si NMR (C$_6$D$_6$, 303 K) δ 0.46 (J_{SiH} = 147 Hz).

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