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Decamethyltitanocene hydride intermediates in the hydrogenation of the corresponding titanocene-(η^2 -ethene) or (η^2 -alkyne) complexes and the effects of bulkier auxiliary ligands†

Jiří Pinkas,^a Róbert Gyepes,^{b,c} Ivana Císařová,^c Jiří Kubišta,^a Michal Horáček^a and Karel Mach *^a

¹H NMR studies of reactions of titanocene [Cp*₂Ti] (Cp* = η^5 -C₅Me₅) and its derivatives [Cp*(η^5 : η^1 -C₅Me₄CH₂)TiMe] and [Cp*₂Ti(η^2 -CH₂=CH₂)] with excess dihydrogen at room temperature and pressures lower than 1 bar revealed the formation of dihydride [Cp*₂TiH₂] (**1**) and the concurrent liberation of either methane or ethane, depending on the organometallic reactant. The subsequent slow decay of **1** yielding [Cp*₂TiH] (**2**) was mediated by titanocene formed *in situ* and controlled by hydrogen pressure. The crystalline products obtained by evaporating a hexane solution of fresh [Cp*₂Ti] in the presence of hydrogen contained crystals having either two independent molecules of **1** in the asymmetric part of the unit cell or cocrystals consisting of **1** and [Cp*₂Ti] in a 2 : 1 ratio. Hydrogenation of alkyne complexes [Cp*₂Ti(η^2 -R¹C≡CR²)] (R¹ = R² = Me or Et) performed at room temperature afforded alkanes R¹CH₂CH₂R², and after removing hydrogen, **2** was formed in quantitative yields. For alkyne complexes containing bulkier substituent(s) R¹ = Me or Ph, R² = SiMe₃, and R¹ = R² = Ph or SiMe₃, successful hydrogenation required the application of increased temperatures (70–80 °C) and prolonged reaction times, in particular for bis(trimethylsilyl)acetylene. Under these conditions, no transient **1** was detected during the formation of **2**. The bulkier auxiliary ligands η^5 -C₅Me₄^tBu and η^5 -C₅Me₄SiMe₃ did not hinder the addition of dihydrogen to the corresponding titanocenes [(η^5 -C₅Me₄^tBu)₂Ti] and [(η^5 -C₅Me₄SiMe₃)₂Ti] yielding [(η^5 -C₅Me₄^tBu)₂TiH₂] (**3**) and [(η^5 -C₅Me₄SiMe₃)₂TiH₂] (**4**), respectively. In contrast to **1**, the dihydride **4** did not decay with the formation of titanocene monohydride, but dissociated to titanocene upon dihydrogen removal. The monohydrides [(η^5 -C₅Me₄^tBu)₂TiH] (**5**) and [(η^5 -C₅Me₄SiMe₃)₂TiH] (**6**) were obtained by insertion of dihydrogen into the intramolecular titanium-methylene σ -bond in compounds [(η^5 -C₅Me₄^tBu)(η^5 : η^1 -C₅Me₄CMe₂CH₂)Ti] and [(η^5 -C₅Me₄SiMe₃)(η^5 : η^1 -C₅Me₄SiMe₂CH₂)Ti], respectively. The steric influence of the auxiliary ligands became clear from the nature of the products obtained by reacting **5** and **6** with butadiene. They appeared to be the exclusively σ -bonded η^1 -but-2-enyl titanocenes (**7**) and (**8**), instead of the common π -bonded derivatives formed for the sterically less congested titanocenes, including [Cp*₂Ti(η^3 -(1-methylallyl))] (**9**). The molecular structure optimized by DFT for compound **1** acquired a distinctly lower total energy than the analogously optimized complex with a coordinated dihydrogen [Cp*₂Ti(η^2 -H₂)]. The stabilization energies of binding the hydride ligands to the bent titanocenes were estimated from counterpoise computations; they showed a decrease in the order **1** (–132.70 kJ mol^{–1}), **3** (–121.11 kJ mol^{–1}), and **4** (–112.35 kJ mol^{–1}), in accordance with the more facile dihydrogen dissociation.

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^aJ. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic. E-mail: karel.mach@jh-inst.cas.cz

^bDepartment of Chemistry, Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovak Republic

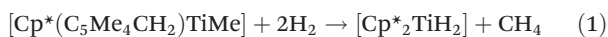
^cDepartment of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

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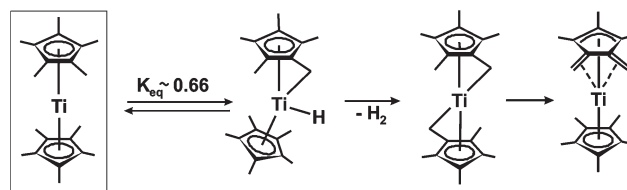
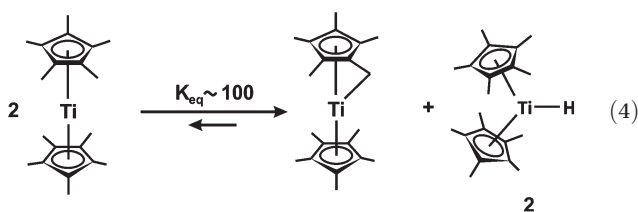
Introduction

The gradual development of opinions on dihydrogen activation and on various modes of its interaction with transition metals, as well as the role of transition metal hydrides in the hydrogenation of organic substrates during the past 50 years, has been reviewed by G. J. Kubas¹ and by the recent state-of-art article by R. H. Crabtree² in a special issue of *Chemical Reviews* devoted to various aspects of dihydrogen activation. The notable absence of group IVB early transition metal (Ti, Zr,

and Hf) metallocenes in considering the binding of molecular hydrogen might reflect both the difficulties in obtaining the d^2 metallocenes containing empty d_σ and filled d_π suitable to combine with $H_2(\sigma)$ and $H_2(\sigma^*)$ orbitals,³ and/or the high electropositivity of these metals with their Pauling electronegativity indexes of 1.5, 1.3 and 1.3,⁴ preferring the formation of hydrides. Actually, the thermally stable Zr and Hf decamethylmetallocene dihydrides $[Cp^*_2ZrH_2]$ ⁵ and $[Cp^*_2HfH_2]$ ⁶ are already known and have been properly characterized. Their reactivity towards olefins and alkynes is also clearly understood. The subsequent regular insertion of double or triple bonds into their M–H bonds afforded clean metallocene hydride-alkyls or -alkenyls and dialkyls or dialkenyls.⁷ For titanium, various synthetic pathways to titanocene and their hydrides as depending on the substituents of titanocene auxiliary ligands were mentioned by J. P. Chirik in an overview on low-valent nitrogen titanocene complexes,⁸ and a full account on early transition metal hydride complexes was reported in 2002 by A. J. Hoskin and D. W. Stephan.⁹ In contrast to the above mentioned Zr and Hf dihydrides, the decamethyltitanocene analogue $[Cp^*_2TiH_2]$ (**1**) was found to be unstable in its solution at ambient temperatures; its decomposition to titanocene $[Cp^*_2Ti]$ and dihydrogen was suggested.^{10a,b} The subsequent study of the hydrogenation of the singly tucked-in titanocene methyl $[Cp^*(C_5Me_4CH_2)TiMe]$ revealed that a rapid uptake of 2 molecules of hydrogen resulting in elimination of methane was followed by a slower liberation of a half equivalent of dihydrogen. This explanation suggested the formation of **1** (eqn (1)) followed by its partial dehydrogenation yielding titanocene $[Cp^*_2Ti]$ (eqn (2)), which comproportionated with the remaining **1** to yield the final $[Cp^*_2TiH]$ (**2**) (eqn (3)).^{10c}



All the species appearing in this system have been assigned their ¹H NMR chemical shifts, and X-ray single crystal structures were determined for **2**¹¹ and for decamethyltitanocene in the co-crystal with its monochloride $[Cp^*_2Ti/Cp^*_2TiCl]$ (1 : 1).¹² The above system is actually more complicated due to the instability of $[Cp^*_2Ti]$, which disproportionates to paramagnetic **2** and singly tucked-in titanocene $[Cp^*(\eta^5:\eta^1-C_5Me_4CH_2)Ti]$ (equilibrium (4))¹² and rapidly tautomerizes to the diamagnetic singly tucked-in titanocene hydride $[Cp^*(\eta^5:\eta^1-C_5Me_4CH_2)TiH]$.^{10b} Upon aging, the tautomer spontaneously dehydrogenates to give

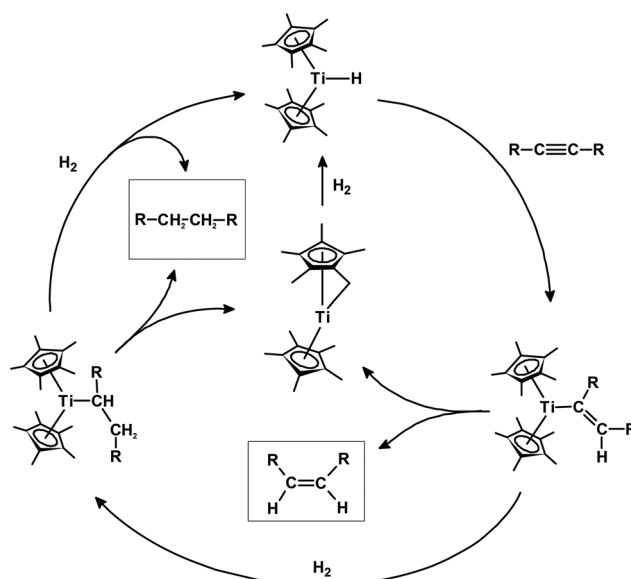


Scheme 1 Tautomerization of decamethyltitanocene and its decay.¹²

transient diamagnetic symmetrical doubly tucked-in titanocene $[(\eta^5:\eta^1-C_5Me_4CH_2)_2Ti]$ which further isomerizes to final doubly tucked-in titanocene having vicinal *exo*-methylene groups $[Cp^*(\eta^3:\eta^4-C_5Me_3(CH_2)_2)Ti]$ (Scheme 1).^{12,13}

The monohydride **2** has been shown to be an excellent hydrogen transfer agent in hydrogenations of unsaturated hydrocarbons acting in a cycle with $[Cp^*(\eta^5:\eta^1-C_5Me_4CH_2)Ti]$ (Scheme 2)¹⁴ and taking part in thermal decomposition of alkyltitanocenes.¹⁵

Among other known titanocenes, bis(1,3-di-*tert*-butylcyclopentadienyl)titanium $[(1,3-tBu_2C_5H_3)_2Ti]$ and $[(C_5Me_4^iPr)_2Ti]$ were reported to react with dihydrogen at low temperatures to give titanocene dihydrides $[(1,3-tBu_2C_5H_3)_2TiH_2]$ ¹⁶ and $[(C_5Me_4^iPr)_2TiH_2]$ ¹⁷ which differed by thermal stability and reactivity. On warming their solutions to ambient temperature and degassing, the former cleanly dissociated to dihydrogen and the titanocene whereas the latter gave rise to the monohydride $[(C_5Me_4^iPr)_2TiH]$,¹⁷ similarly to **1**. The former dihydride $[(1,3-tBu_2C_5H_3)_2TiH_2]$ was obtained from hexane solution at -80 °C as dark red crystals that were stable under vacuum and melted at 152–154 °C.¹⁶ For both dihydrides their ¹H NMR spectra were determined at low temperature in the absence of their parent titanocenes. Following these achievements a thorough investigation of the formation of **1** and its properties



Scheme 2 Hydrogenation of internal alkynes mediated by $[Cp^*_2TiH]$.¹⁴

and the effects of its yet bulkier cyclopentadienyl auxiliary ligands on the properties of titanocene hydride is to be sought.

Herein we report on the detailed studies of dihydrogen reactions carried out under mild conditions (22–70 °C, <1 bar) with $[\text{Cp}^*_2\text{Ti}]$, $[\text{Cp}^*(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)\text{TiMe}]$, **2**, $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-ethene})]$ and a number of titanocene- $(\eta^2\text{-alkyne})$ complexes, with particular attention paid to the formation of transient titanocene dihydride species. The effects of bulky auxiliary ligands $\eta^5\text{-C}_5\text{Me}_4\text{tBu}$ or $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3$ on the stability of the corresponding titanocene dihydrides and on the structure of the products of butadiene addition to the titanocene monohydrides are also investigated.

Results and discussion

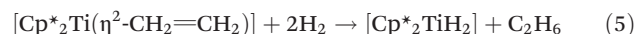
Reaction of hydrogen with $[\text{Cp}^*_2\text{Ti}]$, $[\text{Cp}^*(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2)\text{TiMe}]$, and $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)]$

Admission of dihydrogen (~4.2 mmol) to titanocene $[\text{Cp}^*_2\text{Ti}]$ (0.2 mmol) in toluene- d_8 (1.0 mL) caused an immediate change of its light green color ($\lambda_{\text{max}} \sim 630$ nm) to yellow-brown, while the complete disappearance of its paramagnetic resonance at 63.8 ppm ($\Delta\nu_{1/2} = 170$ Hz) in the broad-range ^1H NMR spectrum was observed. The latter signal was replaced by a dominant broad resonance at $\delta_{\text{H}} 1.90$ ppm ($\Delta\nu_{1/2} = 60$ Hz) accompanied by a weaker one at $\delta_{\text{H}} 3.37$ ppm ($\Delta\nu_{1/2} \sim 70$ Hz) and a weak resonance at $\delta_{\text{H}} 23.0$ ppm ($\Delta\nu_{1/2} = 170$ Hz) due to **2**.^{10c,11,14} The dominant resonance occurred at the chemical shift found by Brintzinger *et al.*^{10b} in the same reacting system and was assigned to the Cp* methyls of **1**. However, we could not find any signal at 0.28 ppm in our spectra, which was assigned by them to the hydride nuclei. Since the integral intensity ratio of the signals at 1.90 ppm and 3.37 ppm was close to 15 and the signals displayed only marginal changes in their chemical shifts upon decreasing the sample temperature to -45 °C, we have assigned the resonance at 3.37 ppm to the hydride moieties of diamagnetic $[\text{Cp}^*_2\text{TiH}_2]$. Concurrently, the signal at 1.90 ppm narrowed down to give $\Delta\nu_{1/2} = 16$ Hz, which allowed the measurement of the ^{13}C NMR resonance signals at δ_{C} (C_5Me_5) 13.34 ppm and δ_{C} (C_5Me_5) at 119.79 ppm (see Fig. S1 and S2 in the ESI†). On aging, the above solution showed a steady, slow increase in the signal intensity of **2**, at the expense of both resonances of **1**, giving approximately 60% of **2** and 40% of **1** after 3 months at room temperature. Unfortunately, the expected increase in dihydrogen concentration could not be monitored by ^1H NMR spectroscopy, because the resonance of dihydrogen at $\delta_{\text{H}} 4.50$ ppm (*cf.* ref. 18) was quenched by traces of both hydrides, apparently due to exchanges causing a large signal broadening. In contrast, the paramagnetic $[\text{Cp}^*_2\text{TiCl}]$, used as a signal intensity standard in most of the investigated systems, did not affect the dihydrogen signal.

The analogous hydrogenation of thermally stable $[\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2)\text{TiMe}]$ afforded virtually identical resonances for both the major **1** and the minor **2** products. In addition, the

intensity of the methane signal at $\delta_{\text{H}} 0.17$ ppm (*cf.* ref. 18) proved that methane elimination was already accomplished before acquiring the first ^1H NMR spectrum 30 minutes after adding hydrogen, as the signal intensity showed no increase with later measurements. The progress of hydrogenating $[\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2)\text{TiMe}]$ was also followed by measuring its electronic absorption spectra in the visible region, taking advantage of its thermal stability in comparison with that of $[\text{Cp}^*_2\text{Ti}]$.¹² The dark green color of the reagent ($\lambda_{\text{max}} = 607$ nm)¹⁹ turned brownish-yellow after about 30 min, which allowed assigning the new absorption band at 483 nm to **1**. After degassing and aging for 5 days, the color of the solution turned reddish-ochre, displaying an absorption band at 477 nm and a shoulder at 550 nm, which was in agreement with data of Andersen *et al.*¹¹ for **2** (for visible spectra see the ESI†).

^1H NMR monitoring of the hydrogenation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)]$ ²⁰ revealed that reaction (5) was accomplished in 10 minutes upon warming the frozen solution to room temperature (see Fig. S3 and S4 in the ESI†).



^1H NMR signals of the reagent disappeared and that of ethane at $\delta_{\text{H}} 0.81$ ppm (*cf.* ref. 18) did not grow further. The approximate composition of titanocene products – $[\text{Cp}^*_2\text{Ti}]$ 10%, **1** 88%, and **2** 2% showed that the dihydrogen in solution was substituted by ethane, since the titanocene resonance could not be observed in the presence of the dihydrogen. After 40 min the titanocene signal disappeared, whereas that of **2** grew in intensity at the expense of the signals of **1** appearing at 1.88 ppm and 3.37 ppm. With continuing conversion of **1** to **2** the former signal shifted to 1.91 ppm and turned narrower ($\Delta\nu_{1/2} = 10$ Hz), whereas the latter broadened so that it became imperceptible. The latter effect can be attributed to an extensive exchange of the both hydrides with dihydrogen, whose concentration should be increasing upon conversion of **1** to **2** (*via* eqn (2) followed by eqn (3) or eqn (4)). After 3 months this system yielded an approximate equilibrium composition of **2** (65%) and **1** (35%), similar to the above mentioned systems. In all these hydrogenated systems the subsequent formation of **2** was accelerated by removing free dihydrogen under vacuum, apparently shifting the equilibrium (2) to the right side, thus supplying more $[\text{Cp}^*_2\text{Ti}]$ for comproportionation with **1** (eqn (3)) and/or its disproportionation (eqn (4)). A rapid degassing of the reaction solution resulted even in transient recovery of $[\text{Cp}^*_2\text{Ti}]$, whose signal at 63.8 ppm was observed for approximately 10 min. The full conversion of **1** to **2** was achieved after complete dihydrogen removal by twice repeating the freezing/thawing cycle under vacuum.

The above results were complemented by the discovery that the signal of **1** at 1.91 ppm occurred after adding dihydrogen to a toluene- d_8 solution of **2**, its area amounting to about 10% of the signal area of **2** at 23.0 ppm. Measurements of this sample between -45 °C and +65 °C showed that the signals at 3.37 ppm and 1.90 ppm were clearly observed at the lowest

temperature; however, the former broadened with increasing temperature, becoming invisible at 25 °C and the latter shifted slightly at this temperature to 1.91 ppm. Upon increasing the temperature further, the latter signal broadened strongly and moved to lower magnetic fields to coalesce finally into one broad signal at about 2.6 ppm at 65 °C (see Fig. S5 and S6 in the ESI†). This coalescence apparently resulted from exchanges involving the hydrides, the Cp* methyl hydrogen atoms and dihydrogen, which are known to proceed effectively during deuteration of **2**.¹¹

An overview of the reactions of titanocene reagents with excess dihydrogen followed by ¹H NMR is depicted in Scheme 3. Concerning the reaction mechanism, the bent titanocene derivatives [Cp*(C₅Me₄CH₂)TiMe] and [Cp*₂Ti(η²-C₂H₄)] should coordinate dihydrogen which upon insertion into the Ti–C bond(s) would yield titanocene and methane or ethane, respectively. In particular, titanocene itself reacted with hydrogen immediately and completely as evident from the absence of its signal at 63.8 ppm and the absence of its tautomer resonance at 2.19 ppm. Apparently, both the bent titanocene tautomer and the parallel titanocene are capable of coordinating dihydrogen and then accomplishing the oxidative addition rearrangement to **1**. A slow conversion of **1** to **2** which runs to equilibrium composition depending on hydrogen pressure should be mediated by titanocene although its equilibrium concentration was either very low or its ¹H NMR signal was unobservable due to its broadening, e.g. due to exchanges between the titanocene containing the coordinated dihydrogen [Cp*₂Ti(H₂)] and dihydrogen. Under consideration is the disproportionation of titanocene according to equilibrium (4) which in the presence of dihydrogen would yield only **2** due to dihydrogen addition to [Cp*(C₅Me₄CH₂)Ti].¹⁴ Such an equilibrium for pure **2** contained trace amounts of [Cp*₂Ti] and [Cp*(C₅Me₄CH₂)Ti] detectable in amplified ¹H NMR spectra, however, only in the strict absence of dihydrogen. The other possibility is the comproportionation of [Cp*₂Ti] with **1**

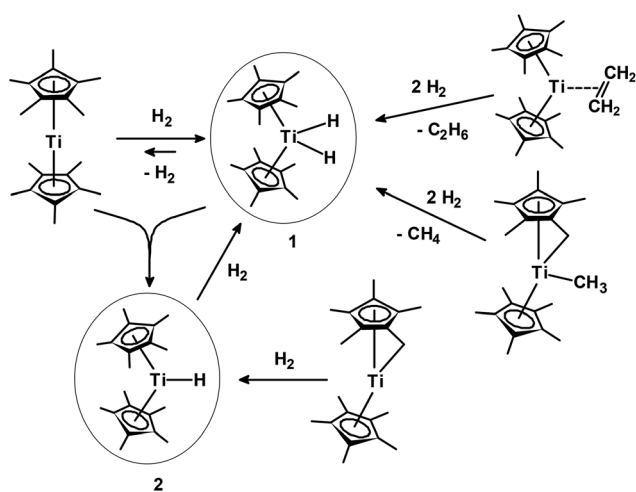
as suggested by eqn (3).^{10c} The steric hindrance for this bimolecular reaction could be partially relieved by reacting with the bent titanocene tautomer. The viability of the comproportionation reaction was supported by obtaining evidence that a similar sterically demanding reaction between excess [Cp*₂Ti] and [Cp*₂Ti(η²-C₂H₄)] gave rise to [Cp*(C₅Me₄CH₂)Ti] and ethane, until all the ethene complex was consumed. Only then the remaining [Cp*₂Ti] disproportionated (eqn (4)) to give [Cp*(C₅Me₄CH₂)Ti] and **2**, whose formation was clearly detected by the δ_H 23.0 ppm signal (see Fig. S7 and S8 in the ESI†).

The addition of dihydrogen to **2** which generates **1** is evidently a retro-process involving equilibrium (4) and a high affinity of titanocene to dihydrogen. The retro-reaction (3) is difficult to realize since the disproportionation of two molecules of **2** should be initiated by dihydrogen addition. There are no signs of dimerization of **2** alone¹¹ and no evidence of interaction of **2** with dihydrogen from ¹H NMR spectra; the paramagnetic shift of its resonance at 23.0 ppm (25 °C) and linewidth did not change in the presence of dihydrogen in the range from –45 to +65 °C (cf. Fig. S9 and S10 with S5 and S6 in the ESI†).

The surprising thermal stability of **1** in the solid state was established in the ocher-orange crystalline material obtained after admission of hydrogen to a hexane solution of [Cp*₂Ti] followed by slow distillation of the solvent under a hydrogen atmosphere to a trap cooled by liquid nitrogen. The X-ray single crystal analysis of selected orange plates revealed two crystal entities. The first fraction of crystals, obtained when maintaining the evaporated solution at –5 °C, contained two independent molecules of **1** in the asymmetric part of the unit cell (crystal **A**). The second fraction (crystal **B**), which was obtained by evaporation at room temperature, yielded cocrystals of **1** and [Cp*₂Ti] in a 2 : 1 ratio. The important geometric parameters of the different molecules of **1** and DFT optimized structures of the dihydride and the titanocene-dihydrogen complex are listed in Table 1.

Although the data for the hydride atoms – which all were localized on Fourier maps – show a mediocre precision in determining their position, their comparison with the data of molecules optimized by DFT methods nonetheless excludes the possibility that these hydrogen atoms might belong to a titanocene-dihydrogen complex. All the dihydride molecules are contaminated with an admixture of [Cp*₂TiCl] (see the Experimental section). The titanocene molecule in crystal **1B** showed parallel cyclopentadienyl rings with the Ti–Cg distance of 2.0021(11) Å, which is slightly longer than the distance of 1.983(2) Å found in the co-crystal of [Cp*₂Ti] and [Cp*₂TiCl] (1 : 1) (Fig. 1).¹²

Crystalline samples of the same appearance as the above single crystals were subjected for melting point determination in sealed capillaries under argon. They softened at 155 °C (**1A**) and at 165 °C (**1B**) and both slowly sublimed onto the capillary walls. ¹H NMR spectra of average crystalline samples (**1A/1B**) in toluene-*d*₈ revealed the following composition: [Cp*₂Ti] together with its tautomer 12%/24%, **2** 13%/9%, and **1** 75%/



Scheme 3 Reactions of decamethyltitanocene and its derivatives with hydrogen.

Table 1 Selected interatomic distances (Å) and bond angles (°) for crystals **1A** and **1B** and DFT-computed optimized Cp*₂TiH₂ and Cp*₂Ti(η²-H₂) molecules

Crystal Molecule	1A		1B 1 ^a	DFT optimized structure	
	1	2		Cp* ₂ TiH ₂	Cp* ₂ Ti(η ² -H ₂)
Ti-Cg(1) ^b	2.0414(10)	2.0426(10)	2.0392(12)	2.024	1.979
Ti-Cg(2) ^b	2.0391(9)	2.0372(11)	2.0337(13)	2.028	1.981
Ti-Pl(1) ^c	2.0414(8)	2.0391(8)	2.0388(11)	—	—
Ti-Pl(2) ^c	2.0391(8)	2.0424(8)	2.0334(12)	—	—
Ti-H(1A)	1.63(3)	1.59(4)	1.88(4)	1.730	1.799
Ti-H(1B)	1.68(3)	1.66(4)	1.76(4)	1.727	1.803
H(1A)-H(1B)	2.31(4)	2.13(5)	1.58(9)	2.467	0.911
Cg(1)-Ti-Cg(2) ^b	149.24(4)	148.56(4)	149.22(5)	147.909	155.265
H(1A)-Ti-H(1B)	88.9(14)	82(2)	51(3)	91.066	29.289
φ ^d	29.93(9)	30.3(8)	28.7(2)	—	—

^a Symmetry operation used to generate equivalent positions: 1 - x, -y + 2, -z + 1. ^b Cg(1) and Cg(2) denote the centre of gravity of the cyclopentadienyl rings. ^c Cyclopentadienyl ring least-squares planes containing the center of gravity having the same numeral label. ^d Angle between the least-squares planes of cyclopentadienyl rings.

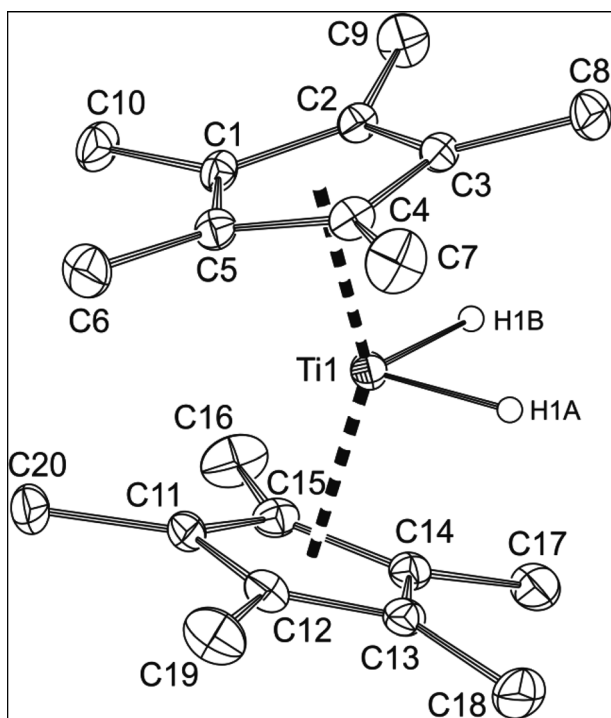


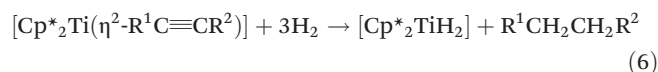
Fig. 1 PLATON drawing of [Cp*₂TiH₂] (crystal **1A**, molecule **1**) at the 30% probability level and with the atom labeling scheme. Hydrogen atoms except the hydrides and the disordered chloride atom are omitted for clarity.

67% after 40 min of aging at room temperature, the period required for sample preparation. The infrared spectra of the average crystalline samples in KBr pellet were very similar, showing an absorption band at 1560 cm⁻¹ and a shoulder at 1586 cm⁻¹ of medium intensity, in general accordance with the initial report for [Cp*₂TiH₂].^{10b} Their lower intensity compared with the IR spectrum of **2**, which showed a very strong band at 1509 cm⁻¹ for the valence Ti-H vibration accounts for

a decreased content of **1** indicated both by the crystal structure and by ¹H NMR measurement.

Hydrogenation of Cp*₂Ti(η²-R¹C≡CR²) complexes

Decamethyltitanocene-alkyne complexes [Cp*₂Ti(η²-R¹C≡CR²)]²¹ (0.3–0.5 mmol) in toluene-*d*₈ (4.0 mL) were hydrogenated with at least 4.2 mmoles of gaseous dihydrogen in a constant volume. This hydrogen amount thus always surpassed the stoichiometry for the conversion of organic ligands attached to titanium to corresponding alkanes and formation of **1** (eqn (6)).



The kinetics of hydrogen consumption was not followed; the hydrogenation was terminated by vacuum distillation of all volatiles into a liquid nitrogen-cooled trap after the typical ochre-red color of **2** appeared and did not change further visually for the last third of the total reaction time. Organic products were separated by vacuum distillation at temperatures never exceeding 80 °C and were analyzed by GC-MS and/or ¹H and ¹³C NMR spectroscopy (see the ESI[†]). The residue was dissolved in toluene-*d*₈ and analyzed by broad range ¹H NMR spectroscopy always displaying the overwhelming broad resonance of paramagnetic **2** at 23.0 ppm at 25 °C. The course of hydrogenation was found to depend strongly on the nature of the alkyne substituents, presumably on their bulkiness. Whereas the 2-butyne and 3-hexyne complexes were hydrogenated at room temperature within 8 h, the analogues containing phenyl, and especially trimethylsilyl substituent(s) required heating to 70 °C for a prolonged reaction time. However, the hydrogenation of [Cp*₂Ti(η²-Me₃SiC≡CSiMe₃)]^{21c} was not accomplished even after 112 h at 80 °C (Table 2).

The hydrogenation of [Cp*₂Ti(η²-PhC≡CPh)] and [Cp*₂Ti(η²-Me₃SiC≡CSiMe₃)] was also followed by ¹H NMR spectra. About one half of the former complex was converted after 1 h

Table 2 Hydrogenation of Cp*₂Ti(R¹C≡CR²) complexes^a

R ¹	R ²	Temperature (°C)	Time (h)	Conversion to 2 (%)	Organic product ^b	Conversion (%)
Me	Me	22	4	100	Me(CH ₂) ₂ Me	100
Et	Et	22	8	100	Me(CH ₂) ₄ Me	100
Ph	Ph	22	12	5	Not determined	—
		70	32	100	Ph(CH ₂) ₂ Ph	100
Ph	SiMe ₃	70	32	100	Ph(CH ₂) ₂ SiMe ₃	100
Me	SiMe ₃	70	48	100	Me(CH ₂) ₂ SiMe ₃	100
SiMe ₃	SiMe ₃	80	112	87	Me ₃ Si(CH ₂) ₂ SiMe ₃ ^c	45

^a Excess dihydrogen (~4.2 mmol) was admitted to the reagent (0.3–0.5 mmol) in toluene-*d*₈ (1.0 mL) in a constant volume. ^b Volatile organic products were vacuum-distilled together with toluene-*d*₈ and analyzed by ¹H and ¹³C NMR spectra and the GC-MS method. ^c A mixture with 1,2-bis(trimethylsilyl)ethene (*E*-) 50%, (*Z*-) 5%.

at room temperature into **1** (δ_{H} 1.88 ppm ($\Delta\nu_{1/2}$ = 65 Hz) and 3.37 ppm ($\Delta\nu_{1/2}$ = 46 Hz)) and *cis*-stilbene (δ_{H} 6.43 ppm), whereas only a trace of **2** was observed. After 72 h at room temperature the reagent hydrogenation was accomplished yielding overwhelming amounts of **2** and *cis*-stilbene. Heating the mixture to 100 °C for 1 h resulted in hydrogenation of the majority of *cis*-stilbene to 1,2-diphenylethane whereas no decay was noticed for **2** (see Fig. S11 and S12 in the ESI†). The absence of a [Cp*(C₅Me₄CH₂)Ti] signal at δ_{H} –11.7 ppm indicated that the hydrogenation was run with dihydrogen and **2** participated only as a hydrogen transfer agent.¹⁴

An attempt to shed light on the mechanism of the diphenylacetylene ligand hydrogenation by using dideuterium failed, as the resonance of *cis*-stilbene at 6.43 ppm did not reveal a recognizable presence of deuterated species. However, the signal of [Cp*₂TiH₂] at 3.45 ppm appeared to be overlapped with the triplet 1 : 1 : 1 signal of [Cp*₂Ti(*H*)D] showing the *J*_{HD} coupling of ~3.4 Hz that is a typical value of the metal hydride-deuteride species¹ (see Fig. S13 in the ESI†). These results indicate that a considerable part of deuterium underwent rapid exchanges with the Cp* ligands; an assessment of deuterium distribution over the system by a combined GC-MS and NMR study has not yet been attempted.

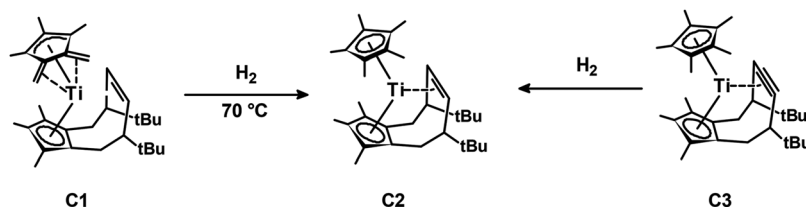
The [Cp*₂Ti(η^2 -Me₃SiC≡CSiMe₃)] complex remained intact after exposure to hydrogen at room temperature for 3 days. At 80 °C the signal of **2** began to grow gradually in time while no signals of **1** were detected. The hydrogenation of the reagent was not accomplished even after 112 h at 80 °C, when the experiment was terminated. The acetylene ligand was hydrogenated to *cis*-alkene, the latter concurrently isomerized to *trans*-alkene, and both were more slowly hydrogenated to the alkane (Table 2).

Hydrogenation of doubly tucked-in titanocenes

It is of practical interest to know whether [Cp*Ti(η^3 : η^4 -C₅Me₃(CH₂)₂)] as the main, thermally stable decay product of [Cp*₂Ti]¹² can be converted by reacting with dihydrogen to catalytically active **2**. Two doubly tucked-in compounds [Cp*Ti(η^3 : η^4 -C₅Me₃(CH₂)₂)]¹³ and [Ti{ η^3 : η^4 -C₅Me₃(CH₂)₂}{ η^5 -C₅Me₃(CH₂CH^tBuCH=CHCH^tBuCH₂)}]²² (**C1**) in toluene-*d*₈ solutions showed no visible change of their blue color after introducing dihydrogen at room temperature within 3 days. This proved that the dehydrogenation of the titanocene tautomer followed by rearrangement to [Cp*Ti(η^3 : η^4 -C₅Me₃(CH₂)₂)] (Scheme 1) is practically irreversible at room temperature. However, heating to 70 °C for 26 h resulted in converting [Cp*Ti(η^3 : η^4 -C₅Me₃(CH₂)₂)] to **2** and compound **C1** to [Cp*Ti{ η^5 : η^2 -C₅Me₃(CH₂CH^tBuCH=CHCH^tBuCH₂)}] (**C2**).^{23a} The latter compound was previously obtained by hydrogenating the intramolecular acetylenic complex [Cp*Ti{ η^5 : η^2 -C₅Me₃(CH₂CH^tBuC≡CCH^tBuCH₂)}] (**C3**) (Scheme 4).^{23b} The structure of product **C2** indicates that the titanocene [Cp*Ti{ η^5 : η^2 -C₅Me₃(CH₂CH^tBuCH=CHCH^tBuCH₂)}] was a transient reaction product which subsequently stabilized by coordinating the intramolecular double bond. Further hydrogenation of **C2** at 80 °C brought about an increased elimination of 2,7-tetramethyloct-4-ene isomers, indicating the hydrogenolysis of the bicyclic ligand.

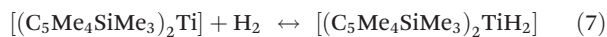
Effects of bulky auxiliary ligands η^5 -C₅Me₄^tBu or η^5 -C₅Me₄SiMe₃ on the stability of titanocene dihydrides and on the structure of the products of addition of butadiene to titanocene monohydrides

Replacement of one methyl group on each Cp* ligand by the more bulky *t*-butyl or trimethylsilyl group was previously

**Scheme 4** Hydrogenation of doubly tucked-in titanocene **C1** and the other precursor **C3** to **C2**.

shown to change the reactivity of titanocenes towards dinitrogen,²⁴ CO, NH₃, and Me₃SiN₃,¹⁷ and the titanocene-ethene complexes to but-2-yne,¹² apparently due to the increased sterical congestion in the bent titanocene moiety. Both titanocenes, the brown [(C₅Me₄^tBu)₂Ti]^{12,24} and the green [(C₅Me₄SiMe₃)₂Ti]^{25a} indicated their reaction with hydrogen by the immediate change of their colors to ocher. ¹H NMR spectra revealed the presence of minor signals of the titanocene monohydrides as impurities (see below) and broad signals at about 0–3 ppm likely due to expected dihydrides [(C₅Me₄^tBu)₂TiH₂] (3) and [(C₅Me₄SiMe₃)₂TiH₂] (4). These resolved at –35 °C into single resonances for the TiH₂ moiety, one pair of singlets for two different methyl groups on the cyclopentadienyl ring C₅Me₄ and one singlet due to the CMe₃ or SiMe₃ group in the order of decreasing δ_H and in appropriate intensity ratios. Their ¹³C NMR spectra were also obtained as seven and six singlets, respectively (see Fig. S14–S16 in the ESI†).

Simultaneously with 4 the considerable presence of [(C₅Me₄SiMe₃)₂Ti] was also established from its outmost low magnetic field resonance at 99.6 ppm (Fig. 2) implying an equilibrium (7) whose composition depended on the hydrogen pressure.



An extensive hydrogen exchange within this equilibrium apparently gave rise to the broad signal at 1.6 ppm observed at 25 °C (Fig. 3).

The composition of this ocher solution did not change even after aging at room temperature for 6 months. Degassing of this solution restored the original brownish-green color, and the ¹H NMR spectrum showed the dominant [(C₅Me₄SiMe₃)₂Ti] and an admixture of [(C₅Me₄SiMe₃)₂TiH] only. The latter compound thus arose from hydrogenation of

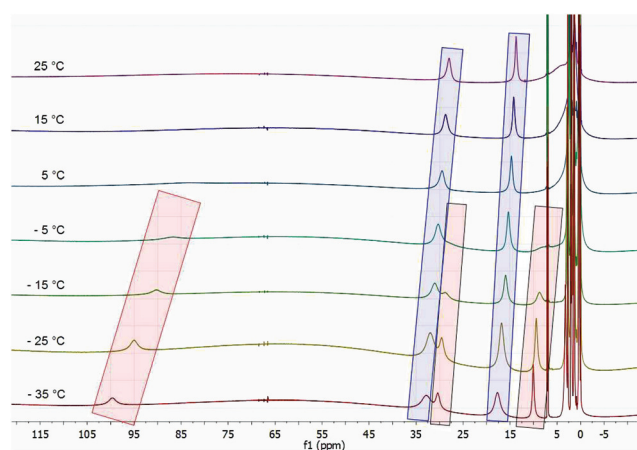


Fig. 2 ¹H NMR spectra observed after addition of hydrogen to a mixture of [(C₅Me₄SiMe₃)₂Ti] and [(C₅Me₄SiMe₃)Ti(C₅Me₄SiMe₂CH₂)] in toluene-*d*₈ measured at temperatures from –35 to 25 °C. Signals of [(C₅Me₄SiMe₃)₂Ti] and [(C₅Me₄SiMe₃)₂TiH] (6) as depending on temperature are highlighted by red and blue bars, respectively; signals of diamagnetic 4 fall into 0–3 ppm range.

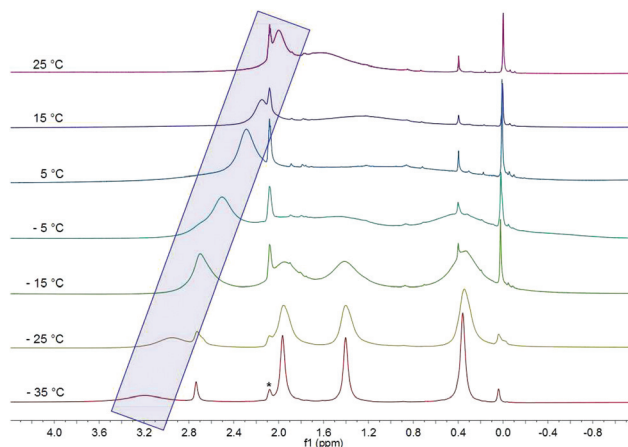


Fig. 3 An expanded region of Fig. 2 demonstrates broadening and subsequent coalescence of ¹H NMR signals of 4 with increasing temperature. The signal highlighted by blue bar corresponds to the SiMe₃ group of [(C₅Me₄SiMe₃)₂TiH] (6). (*) denotes the solvent signal.

[[η⁵-C₅Me₄SiMe₃](η⁵:η¹-C₅Me₄SiMe₂CH₂)Ti] or similar compounds which resulted from thermal treatment of the titanocene,^{25b} and not from the decay of 4, as known for the Cp* system above.

An attempted preparation of [(C₅Me₄SiMe₃)₂TiH(D)] by reacting the titanocene with HD apparently yielded the required compound contaminated with the dihydride, since the integral intensity of the distorted signal at 2.78 ppm was 1.4 instead of the theoretical value 1.0, with respect to the integral value of 12 for each of the two δH (C₅Me₄) signals (see Fig. S17 in the ESI†). The distorted signal was composed of singlet dihydride and triplet 1:1:1 for hydride–deuteride showing the *J*_{HD} coupling of ~6 Hz. This value is compatible with the hydride–deuteride structure since the ¹*J*_{HD} coupling for coordinated molecular HD ranges between 15–35 Hz.^{1,2} This *J*_{HD} coupling is, however, larger than that for [Cp*₂TiH(D)] (3.4 Hz, see above) reflecting thus a weaker calculated Ti–H bonding for 4 with respect to 1 (see below). The signal for 4, of correct intensity, was obtained after aging the sample for 6 months (see Fig. S18 in the ESI†), which indicates that exchanges between hydride/deuteride and methyl hydrogen atoms are markedly slower than *e.g.*, for [Cp*₂TiH].¹¹ This can be caused by the virtual absence of the tucked-in titanocene hydride tautomer for [(C₅Me₄SiMe₃)₂Ti] which likely mediates such exchanges in the [Cp*₂Ti] systems.

The chemical shifts for titanocene dihydrides so far gathered fit into the order of decreasing δ_H (TiH₂) with increasing sterical bulk of substituents on cyclopentadienyl ligands: Me (Cp*) 3.42 (–45 °C) > ⁱPr 3.25 (–75 °C)¹⁷ > ^tBu 3.04 (–35 °C) > SiMe₃ 2.74 ppm (–35 °C). The value of δ_H (TiH₂) 2.62 ppm for [(1,3-^tBu₂C₅H₃)₂TiH₂]¹⁶ can fit this series with regard to the bulkiness of the cyclopentadienyl substituents, however, little is known on the influence of the electron donation ability of auxiliary ligands which should be lower for the less alkylated compound. An analogous effect of the bulkiness of cyclopenta-

Table 3 EPR and UV-vis spectra of titanocene hydrides **2**, **5**, and **6** and products of their reaction with butadiene **7** and **8**

Compound no.	EPR		EPR			UV-vis (nm)		Ref.		
	g_{iso}	ΔH (G)	g_1	g_2	g_3					
			g_{\perp}		g_{\parallel}	g_{av}				
2	— ^a	— ^a	1.975		1.769	1.906	550 ^b	476	—	11
5	— ^a	— ^a	1.980		1.776	1.912	580 ^b	475	375 ^b	This work
6	— ^a	— ^a	1.981		1.806	1.922	580 ^b	475	375 ^b	This work
7	1.956	38	1.997	1.985	1.895	1.959	605 ^b	500	380 ^b	This work
8	1.962	24	2.000	1.985	1.900	1.962	620 ^b	485	—	This work

^a Only EPR spectra of impurities are observable as single lines for Cp*₂TiCl ($g_{\text{iso}} \sim 1.956$, $\Delta H \sim 30$ G) and/or oxo-impurity Cp*₂TiOR ($g_{\text{iso}} \sim 1.977$, $\Delta H = 3\text{--}5$ G, $a(\text{Ti}) = 8\text{--}10$ G). These are observable in frozen toluene glass at common $g_1 \sim 1.999$, $g_2 \sim 1.982$ and specific $g_3(\text{Cp}^*_2\text{TiCl}) \sim 1.888$ (ref. 30 and 31) and $g_3(\text{Cp}^*_2\text{TiOR}) \sim 1.952$ (see the ESI).³² The electronic triplet state impurity $[(\text{Cp}^*_2\text{Ti})_2\text{O}]^{33}$ has been observed in some samples showing the outmost feature $\Delta H_{zz} = 473$ G, $g_{zz} = 1.985$ and $\Delta M_S = 2$ at $g \sim 3.970$ (see the ESI). ^b Shoulder.

dienyl auxiliary ligands inducing a decrease in equilibrium constants for dinitrogen coordination to titanocenes has been reported by Chirik *et al.*²⁶

DFT computations for the presently prepared titanocene dihydrides and titanocene dihydrogen complexes indicated that the dihydride $[\text{Cp}^*_2\text{TiH}_2]$ is by 34.31 kJ mol⁻¹ more stable than the analogous dihydrogen complex $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-H}_2)]$ whereas for the $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}]$ analogues only one half of the energy difference (17.11 kJ mol⁻¹) was found. The counterpoise energies computed between the titanocene fragment and the dihydride atoms correspondingly showed a decrease in the order of auxiliary ligands $\text{Cp}^* > \text{C}_5\text{Me}_4\text{tBu} > \text{C}_5\text{Me}_4\text{SiMe}_3$ (see Table 1 in the ESI†); the difference between edge cases of 20 kJ mol⁻¹ is in accord with the reversible dissociation of hydrogen from an equilibrium mixture of **4** and $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}]$ upon degassing (eqn (7)).

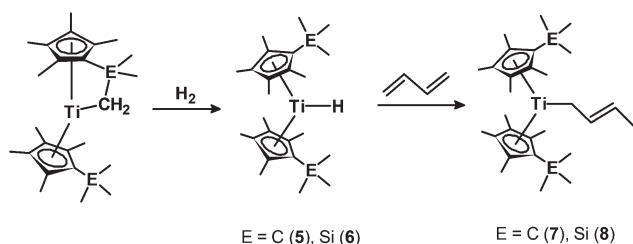
Owing to the low sterical demand of the hydrogen molecule, no sterical hindrance was encountered in preparing titanocene monohydrides by hydrogenation of intramolecular σ -titanium-methylene compounds $[(\eta^5\text{-C}_5\text{Me}_4\text{tBu})(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CMe}_2\text{CH}_2)\text{Ti}]$ (ref. 27) and $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)\text{Ti}]$ (ref. 28) yielding $[(\eta^5\text{-C}_5\text{Me}_4\text{tBu})_2\text{TiH}]$ (**5**) and $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{TiH}]$ (**6**), respectively (Scheme 5). This method was previously used to obtain lanthanide(III) hydride complexes $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2\text{LnH}(\text{THF})]$ (Ln = Y, Nd, Sm, Dy, Lu,^{29a} and Ce^{29b}) and $[(\text{Cp}^*_2\text{CeH})_2]$.^{29c}

The EI-MS spectra of the brown crystalline hydrides **5** and **6** showed molecular ions of low intensity due to the easy elimin-

ation of hydrogen molecule(s). The $[\text{M} - \text{H}_2]^+$ ion was the base peak for **6** whereas $[\text{M} - n\text{H}_2]^+$ ions ($n = 1\text{--}3$) were highly abundant for **5**, the base peak for $n = 3$. ¹H NMR spectra of **5** and **6** revealed a set of three broad signals in an integral ratio 18 : 12 : 12. The assignment of high field signals at 3.5 ppm to CMe_3 of **5** and 2.00 ppm to the SiMe_3 group of **6** was compatible with their intensities. The signals of C_5Me_4 moieties of **5** occurred at 18.3 ppm and 22.7 ppm and those of **6** at 13.7 ppm and 27.91 ppm; the signals of hydrides (TiH) were not found similarly to **2** (see Fig. S19 and S20 in the ESI†). The infrared $\nu(\text{Ti-H})$ vibration occurred as a broad medium-intensity absorption band at 1521 cm⁻¹ for **5** and at 1525 cm⁻¹ for **6**. These bands diminished after exposing the KBr pellets to air, whereas the absorption bands of oxygenated products at 571 cm⁻¹ and 577 cm⁻¹, respectively grew stronger in intensity. The electronic absorption spectra of **5** and **6** were nearly identical and exhibited similarity to the visible spectrum of **2** (476 and 547 nm).¹¹ EPR spectra of **2**, **5**, and **6** in toluene glass displayed extremely anisotropic spectra differing distinctly in their high magnetic field g -tensor component. The shape of anisotropic spectra could be interpreted as arising from the g -tensor of cylindrical symmetry, however, its g_{\perp} value could not be exactly identified because this feature coincided with g_1 and g_2 tensor values of Cp*₂TiL impurities (L mostly Cl or OR). The EPR and UV-vis data for **2**, **5**, and **6** are gathered in Table 3 (for relevant EPR records see the ESI†); the crystal structure of **5** is shown in Fig. 4.

All these data and crystallographic Ti-Cg and Ti-H parameters are in agreement with those for **2**¹¹ and the other well-characterized titanocene hydride $[(\text{C}_5\text{Me}_4\text{Ph})_2\text{TiH}]$ (including the description of EPR spectra for $(\text{C}_5\text{Me}_4\text{Ph})_2\text{TiOR}$ impurity in solution).³⁴ The low precision of determination of the Ti-H bond length from X-ray single crystal diffraction is exemplified on these compounds and **1**, ranging from $1.59(4)$ Å for molecule **2** of **1A** to $1.88(4)$ Å for molecule **1** of **1B** (Table 1).

Introducing excess butadiene to both hydrides **5** and **6** induced a nearly immediate color change from ochre to brown. This indicated at first sight that common π -bonded methylallyl derivatives which are typically purple colored for the sterically less congested titanocenes, including $[\text{Cp}^*_2\text{Ti}(\eta^3\text{-}$

**Scheme 5** Synthesis of **5**, **6**, **7**, and **8**.

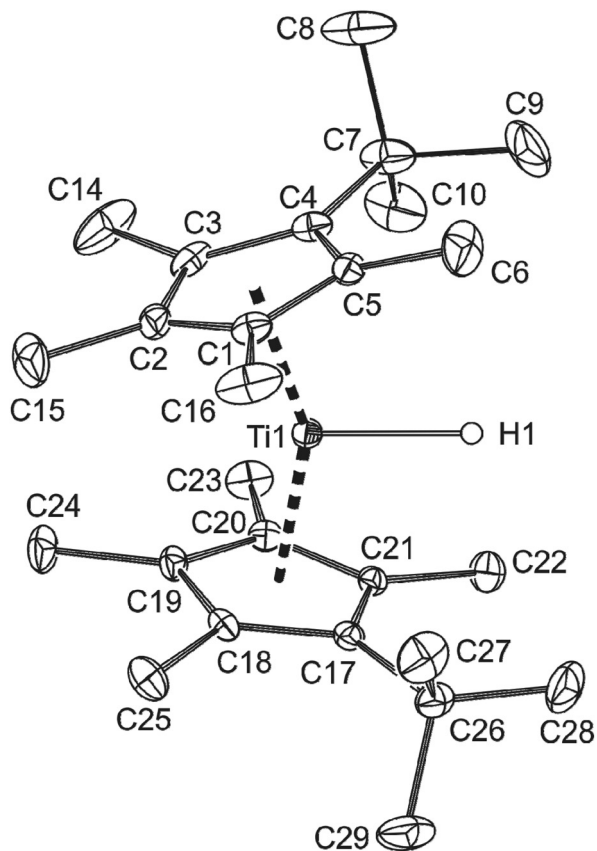


Fig. 4 PLATON drawing of **5** at the 30% probability level, with atom labeling scheme. Hydrogen atoms except the hydride are omitted for clarity. Selected bond distances (Å) and bond angles (°) for molecule 1: Ti–Cg(1) 2.0296(8), Ti–Cg(1) 2.0360(7), Ti–H(1) 1.865(17), Cg(1)–Ti–Cg(2) 152.29(3), Cg(1)–Ti–H(1) 104.9(5), Cg(2)–Ti–H(1) 102.8(5).

(1-methylallyl)] (ref. 14) were not formed. Instead, the σ -bonded η^1 -but-2-enyl derivatives $[(C_5Me_4^tBu)_2Ti(\eta^1-CH_2CH=CHMe)]$ (**7**) and $[(C_5Me_4SiMe_3)_2Ti(\eta^1-CH_2CH=CHMe)]$ (**8**) were obtained in high yields and were characterized by their broad EPR signals at $g_{iso} = 1.958$, $\Delta H = 35$ G and $g_{iso} = 1.962$, $\Delta H = 22$ G, respectively, which resembled those of the corresponding titanocene alkyl³⁰ or alkenyl compounds.³⁵ They also displayed electronic absorption spectra typical of (Cp'_2TiL) compounds (transitions $1a_1 \rightarrow 2a_1$ and $1a_1 \rightarrow b_1$).³⁰ In contrast, $(\eta^3$ -1-methylallyl)titanocenes exhibit narrower EPR signals ($\Delta H \sim 6$ G) at $g_{iso} \sim 1.990$ and a single absorption band in the visible region (518–530 nm).^{14,36} EI-MS spectra of **7** did not show the molecular ion (m/z 457), which eliminated C_4H_7 to give a $[Cp'_2Ti]^+$ fragment, subsequently losing hydrogen and butyl groups similarly to **5**. At variance, EI-MS spectra of **8** displayed a weak molecular ion (m/z 489) losing C_4H_8 to give the $[Cp'_2Ti - H]^+$ base peak. ¹H NMR spectra of **7** and **8** span the range –15 to 15 ppm where three broad signals for methyl groups, two of the tetramethylcyclopentadienyl ring and one of the *t*-Bu or SiMe₃ groups and signals of 2-butenyl groups of much lower intensity and highly varying in linewidth should occur (see Fig. S21 and S22 in the

ESI†). This complexity together with the presence of paramagnetic impurities established by EPR measurements precluded the assignment of spectra. The infrared spectra of both **7** and **8** displayed a weak absorption band at 1629 cm^{-1} apparently due to $\nu(C=C)$ valence vibration. The σ -bonding of 2-butenyl group was established by X-ray single crystal analysis of **8** (Fig. 4). Comparing the basic parameters Cg–Ti–Cg angle $143.19(4)^\circ$ and Ti–Cg distances $2.0985(10)$ Å and $2.0854(10)$ Å with those for $[Cp^*_2Ti(\eta^3$ -1-methylallyl)] (Cg–Ti–Cg $138.15(10)$ – $138.46(11)^\circ$ and Ti–Cg 2.120 – $2.134(3)$ Å for three independent molecules) shows that η^1 - and η^3 -bonding modes of butadiene addition products are controlled by the space in the titanocene shell available for coordination.

Butadiene in excess was also added to toluene-*d*₈ solutions of titanocenes $[(C_5Me_4^tBu)_2Ti]$ and $[(C_5Me_4SiMe_3)_2Ti]$ at room temperature for one day; however, no reaction products were detected by ¹H NMR spectra after evaporation of butadiene to dryness. This is in sharp contrast with the whole class of zirconocene(II) complexes containing the η^4 -1,3-butadiene ligand (largely *s-trans*)^{37a-d} including the persubstituted $[(C_5Me_4Ph)_2Zr(s$ -*trans*- η^4 -buta-1,3-diene)].^{37e} Their formation is facilitated by a larger covalent radius of Zr with respect to Ti by

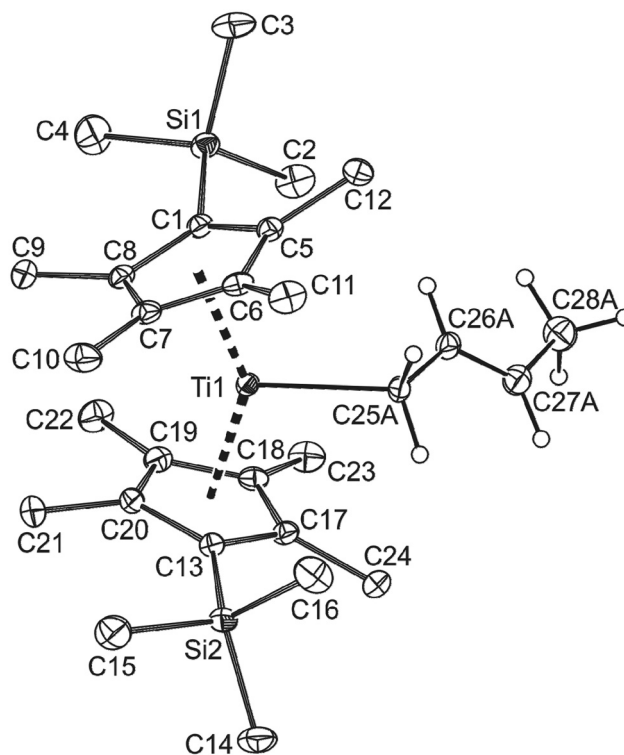


Fig. 5 PLATON drawing of **8** at the 30% probability level, with atom labeling scheme. Hydrogen atoms except those at C25A–C28A are omitted for clarity. Selected bond distances (Å) and angles (°) for molecule 1: Ti–Cg(1) 2.0985(10), Ti–Cg(2) 2.0854(10), Ti–C(25A) 2.225(4), C(25A)–C(26A) 1.504(6), C(26A)–C(27A) 1.326(4), C(27A)–C(28A) 1.489(4), Cg(1)–Ti–Cg(2) $143.19(4)^\circ$, Cg(1)–Ti–C(25A) $106.92(8)^\circ$, Cg(2)–Ti–C(25A) $109.61(9)^\circ$, Ti–C(25A)–C(26A) $107.5(2)^\circ$, C(25A)–C(26A)–C(27A) $129.0(3)^\circ$, C(26A)–C(27A)–C(28A) $125.8(3)^\circ$.

~0.15 Å as well as by a lower Pauling's electronegativity (1.3 for Zr versus 1.5 for Ti) (Fig. 5).⁴

Conclusions

¹H NMR investigations of hydrogenation of decamethyltitanocene [Cp*₂Ti], [Cp*(C₅Me₄CH₂)TiMe], and [Cp*₂Ti(η²-ethene)] revealed that the titanocene dihydride **1** is the primary product which in solution loses hydrogen to give the stable monohydride **2**. The role of titanocene as an intermediate during the latter process is inevitable upon assuming both possible pathways (a) comproportionation of titanocene with the dihydride as previously suggested by Bercaw^{10c} or (b) the titanocene disproportionation according to eqn (4) in the presence of dihydrogen. The conversion of **1** to **2** is accomplished after removal of all dihydrogen; however, admission of dihydrogen induces a reversible process converting Ti(III) **2** to Ti(IV) **1**, apparently *via* a retro-pathway. Unlike in solutions, **1** is stable in crystalline form and its X-ray single crystal structure was determined successfully. Although the precision of hydride atom position determination is low, with the H–H distances appearing in the range 1.58(9)–2.31(4) Å, these were nevertheless incompatible with the H–H distance of 0.911 Å obtained for the DFT-optimized structure of Cp*₂Ti(II) having its dihydrogen molecule η²-coordinated. A larger steric congestion due to η⁵-C₅Me₄^tBu and η⁵-C₅Me₄SiMe₃ auxiliary ligands had no effect on the instant reaction of titanocenes [(C₅Me₄^tBu)₂Ti] and [(C₅Me₄SiMe₃)₂Ti] with hydrogen yielding dihydrides **3** and **4** which were well characterized by ¹H and ¹³C NMR spectra at low temperature. The latter compound formed an equilibrium with [(C₅Me₄SiMe₃)₂Ti] depending on hydrogen pressure while not showing any decay, *e.g.*, to [(C₅Me₄SiMe₃)₂TiH]. Monohydrides **5** and **6** were obtained from hydrogenation of intramolecular σ-titanium-methylene compounds [(η⁵-C₅Me₄^tBu)(η⁵:η¹-C₅Me₄CMe₂CH₂)Ti] and [(η⁵-C₅Me₄SiMe₃)(η⁵:η¹-C₅Me₄SiMe₂CH₂)Ti] and they were used to react with butadiene. The steric effect of auxiliary ligands was manifested by the formation of titanocene (η¹-but-2-en-1-yl) compounds **7** and **8**, whereas decamethyltitanocene binds η³-1-methylallyl, which is a ligand common for sterically less demanding titanocenes.

Experimental section

General considerations

Synthesis, treatment, and subsequent reactions of low-valent titanium compounds were carried out on a vacuum line in sealed all-glass devices equipped with magnetically breakable seals. ¹H (300 MHz), ¹³C (75 MHz) and ²⁹Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in toluene-*d*₈ solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to the residual solvent signal (CD₂H: δ_H 2.08 ppm) and the solvent resonance (*C*_{ipso}: δ_C 137.48 ppm). The δ_{Si} values are related to external tetramethylsilane. EI-MS

spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 10% and by important peaks of lower intensity. Crystalline samples for EI-MS measurements and melting point determinations were placed in glass capillaries in a glovebox Labmaster 130 (mBraun) under purified argon (oxygen and water vapor concentrations were below 2.0 ppm) and sealed with flame. IR spectra of samples in KBr pellets prepared in the glovebox were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm⁻¹. EPR spectra were recorded on a MiniScope MS400 (Magnettech GmbH, Berlin, Germany) equipped with a microwave frequency counter FC 400 and a temperature controller TC H03. UV–near IR spectra in the range 300–2000 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma) and electronically saved. GC-MS analysis was carried out on a Thermo Focus DSQ using a capillary column Thermo TR-5MS (15 m × 0.25 mm × ID 0.25 μm). Elemental analyses were carried out on a FLASH EA1112 CHN/O Automatic Elemental Analyzer (Thermo Scientific). Melting points were measured on a Koffler block in sealed glass capillaries under argon and were not corrected.

Chemicals

The solvents tetrahydrofuran (THF), hexane, and toluene were dried by refluxing over LiAlH₄ and stored as solutions of green dimeric titanocene [(μ-η⁵:η⁵-C₅H₄C₅H₄)(μ-H)₂Ti(η⁵-C₅H₅)₂]³⁸. Toluene-*d*₈ C₇D₈ (99.5% D) (Sigma Aldrich) was degassed, distilled under vacuum on the singly tucked-in permethyltitanocene [Ti(C₅Me₃)(C₅Me₄CH₂)],^{10b} and stored as its solution on a vacuum line. The ethene complexes [Cp*₂Ti(II)(η²-C₂H₄)], [(η⁵-C₅Me₄^tBu)₂Ti(II)(η²-C₂H₄)], and [(η⁵-C₅Me₄SiMe₃)₂Ti(II)(η²-C₂H₄)] were obtained and thermolyzed under vacuum to titanocenes [Cp*₂Ti], [(η⁵-C₅Me₄^tBu)₂Ti] and [(η⁵-C₅Me₄SiMe₃)₂Ti] as reported.¹² Complexes of decamethyltitanocene with internal alkynes but-2-yne, hex-3-yne, 1,2-diphenylethyne, 1-phenyl-2-(trimethylsilyl)ethyne, 1-methyl-2-(trimethylsilyl)ethyne, and 1,2-bis(trimethylsilyl)ethyne were identical to those obtained from [Cp*₂Ti(II)(η²-C₂H₄)] and the alkynes *via* the ligand exchange.^{21a} Compounds [Cp*(C₅Me₄CH₂)TiMe],¹⁹ [(η³:η⁴-C₅Me₃(CH₂)₂)Ti],^{13,39} [(η⁵-C₅Me₄^tBu)(C₅Me₄CMe₂CH₂)Ti],²⁷ [(η⁵-C₅Me₄SiMe₃)(C₅Me₄SiMe₂CH₂)Ti],^{25b,28} and [(η³:η⁴-C₅Me₃(CH₂)₂){η⁵-C₅Me₃(CH₂CH^tBuCH=CHCH^tBuCH₂)}Ti]²² were obtained according to published procedures. A mixture of [Cp*₂Ti] and [Cp*₂Ti(II)(η²-C₂H₄)] was obtained unintentionally by thermolyzing of the latter at 123 °C using a high pumping speed allowing for partial sublimation of non-thermolyzed [Cp*₂Ti(II)(η²-C₂H₄)]. The impurity of Cp*₂TiCl was present in twice crystallized [Cp*₂Ti(II)(η²-C₂H₄)].¹² It was established by EPR (Table 3) and ¹H NMR spectra (14.4 ppm) and used as a spectrum intensity standard since it did not react with hydrogen. Cp*₂TiOR impurities were detected by EPR spectra in very low concentrations (<1% Ti) (Table 3), not reacting with hydrogen. Commercial

hydrogen (anal.3.0) (Messer) and deuterium (Sigma Algrich) were used from steel cylinders without purification. HD was prepared by adding D₂O to LiAlH₄ (see the ESI†).

Reactions of titanocene derivatives with dihydrogen

A three-necked ampule (96 mL) equipped with two magnetically breakable glass seals and a Teflon valve was evacuated to 2×10^{-4} Torr and filled with hydrogen (anal. 3.0) from a steel cylinder after flushing the space around the Teflon valve piston at slightly higher than atmospheric pressure (content of H₂ \geq 4.2 mmol). This ampule was attached *via* a breakable seal to an all-glass T-shape device bearing a three-arm empty ampule (90 mL) and an ampule containing a degassed solution of the titanocene reactant in toluene-*d*₈, typically 0.3–0.5 mmol/1.0–1.5 mL. After evacuating on a vacuum line the T-shape device was sealed off, the solution was transferred to the empty ampule, hydrogen was admitted, and the hydrogenation ampule was kept at 25–80 °C in a water bath for a required time. The hydrogenation ampule could also be torch-sealed off from the T-shape device, containing then at least 1.9 mmol of hydrogen available for hydrogenation. No attempts were made to follow the kinetics of hydrogen consumption. The hydrogenation was terminated by pumping off free hydrogen from a liquid nitrogen-cooled solution. The solution was transferred to an NMR tube under vacuum and the tube was sealed off with a torch. After the NMR analysis was carried out the NMR tube was magnetically broken at the sealed tip under vacuum and the content was collected in a three-necked ampule for vacuum distillation of volatiles for GC-MS and/or ¹H and ¹³C NMR analysis and the isolation of the titanocene product. Hydrogenations as described above were also performed in torch-sealed NMR tubes; a maximum of 0.2 mmol of the reagent in 1.0 mL of toluene-*d*₈ was taken and sealed off, and cooled with liquid nitrogen.

Reaction of [Cp*₂Ti] with dihydrogen to give 1

The titanocene obtained by thermolysis of [Cp*₂Ti(η²-C₂H₄)] at 125 °C under high vacuum¹² was extracted with hexane vapor and the solution was evaporated under vacuum. Crystalline solid (0.07 g, 0.22 mmol) was dissolved in toluene-*d*₈ (1.0 mL) and poured into an NMR tube; hydrogen was admitted, and the tube cooled with liquid nitrogen was sealed off with flame. After warming to room temperature for 10 min the ¹H NMR spectrum shown in Fig. S1 of the ESI† was recorded.

Analytical data for compound 1. ¹H NMR (toluene-*d*₈, 25 °C): 1.90 (br s, Δν_{1/2} = 60 Hz, 30H, C₅Me₅); 3.37 (br s, Δν_{1/2} = 65 Hz, 2H, TiH). ¹H NMR (toluene-*d*₈, -45 °C): 1.87 (br s, Δν_{1/2} = 16 Hz, 30H, C₅Me₅); 3.42 (br s, Δν_{1/2} = 45 Hz, 2H, TiH). ¹³C{¹H} NMR (toluene-*d*₈, -45 °C): 13.34 (C₅Me₅); 119.79 (C₅Me₅).

Preparation of 2 by hydrogenation of [Cp*(η⁵-η¹-C₅Me₄CH₂)TiMe]

A turquoise solution of the crystalline reagent¹⁹ (0.14 g, 0.4 mmol) in toluene-*d*₈ (1.2 mL) was reacted with hydrogen (~4.2 mmol) at room temperature for 8 h. The resulting reddish-ocher solution was degassed and transferred to an

NMR tube. A broad-range ¹H NMR spectrum revealed 2 (23.0 ppm, Δν_{1/2} ~ 170 Hz) contaminated with a trace of [(Cp*₂Ti)₂O] (δ 4.3 ppm, Δν_{1/2} ~ 270 Hz).³³ The eliminated methane was also observed at 0.17 ppm.¹⁸ Volatiles were evaporated to dryness and the residue was extracted with a minimum of hexane and crystallized in a refrigerator. A yield of 0.12 g (95%) reddish-ocher crystalline solid was obtained.

Analytical data for compound 2. EI-MS, ¹H NMR, EPR, IR, and UV-vis data generally agree with ref. 11 and 12.

Hydrogenation of [Cp*₂Ti(η²-C₂H₄)] to 2

(A) Preparative: toluene (4 mL) was added to crystalline [Cp*₂Ti(η²-C₂H₄)] (0.17 g, 0.49 mmol) and hydrogen (~4.2 mmol) from the ampule (96 mL) was admitted *via* an evacuated device. The green color of [Cp*₂Ti(η²-C₂H₄)] began to change to yellow immediately, turning reddish-ocher after 2 h. After stirring for another 3 h the reaction mixture was slowly evaporated to dryness, the residue was dissolved in hexane (3 mL) and crystallized by slow evaporation of the solvent to an ampule arm placed at the cooling wall of a refrigerator. Reddish-ocher crystalline solid was washed out with condensing hexane vapor and dried under vacuum. Yield 0.14 g (89%).

Broad-range ¹H NMR spectra revealed that the dominant broad resonance at δ 23.0 ppm of 2 was accompanied inherently by the titanocene [Cp*₂Ti] resonance at δ 63.8 ppm of very low intensity (≪1%) and a yet weaker resonance at -11.7 ppm typical of [Cp*(C₅Me₄CH₂)Ti].^{10b,15} In addition a weak signal of [(Cp*₂Ti)₂O] at 4.3 ppm (Δν_{1/2} = 270 Hz)³³ was also observable. IR (KBr), EPR and UV-vis spectra are in general accord with published data.^{11,12}

(B) NMR tube experiment: green crystals of [Cp*₂Ti(C₂H₄)] (0.07 g, 0.2 mmol) were dissolved in toluene-*d*₈ (0.8 mL), hydrogen was admitted as above, and a slightly cooled NMR tube was sealed off with a flame. ¹H NMR after 10 min at room temperature: [Cp*₂Ti] δ 63.8 ppm (10%), 2 δ 23.0 ppm (2%), 1 δ 3.37 and 1.88 (Δν_{1/2} 60 Hz) (88%), C₂H₆ δ_H 0.81 ppm (ref. 16) (95%); after 120 min: [Cp*₂Ti] (0%), 2 (23%), 1 δ 3.37 ppm very broad, 1.90 (Δν_{1/2} 12 Hz) (77%), C₂H₆ (100%). After 3 months: 2 (60%), 1 δ 1.91 ppm (40%). The sample after twice repeated degassing 2 (100%), 1 (0%).

Hydrogenation of [Cp*₂Ti(η²-MeC≡CMe)] and Cp*₂Ti(EtC≡Ct)

Admission of gaseous hydrogen (~4.2 mmol) to a dirty green solution of the reactant complex¹⁴ (0.3 mmol) in toluene-*d*₈ (1.0 mL) resulted in a nearly immediate change of its color to reddish-ocher. After stirring for 6 h the reaction solution was degassed, the volatiles were distilled into an NMR tube for analysis, and the residue was dissolved in toluene-*d*₈, and transferred to an NMR tube. Paramagnetic ¹H NMR spectra revealed the presence of 2 (δ_H 23.0 ppm) with [Cp*₂TiCl] (δ_H 14.4 ppm)³⁰ and [(Cp*₂Ti)₂O] (δ_H 4.3 ppm)³³ impurities. ¹H and ¹³C NMR spectra and GC-MS analysis of the volatiles revealed only butane and hexane (see the ESI†).

Hydrogenation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-PhC}\equiv\text{CPh})]$

The reagent preparation, its stoichiometry to hydrogen, and other conditions were the same as in the preceding experiments. The original green color changed to greenish-yellow overnight. The solution was transferred to an NMR tube and assessed to contain only 5% of $[\text{Cp}^*_2\text{TiH}]$. It was then transferred to an ampule and hydrogenated with a new portion of hydrogen (4.2 mmol) at 70 °C for 32 h. The reddish-ocher solution was degassed through a trap cooled with liquid nitrogen and distilled under high vacuum at 70 °C. Volatiles collected in the trap were analyzed by ^1H and ^{13}C NMR spectra to contain 1,2-diphenylethane and a trace of *cis*-stilbene in toluene- d_8 . The toluene- d_8 solution of the residue showed only the signal of **2** at 23.0 ppm.

Hydrogenation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-PhC}\equiv\text{CSiMe}_3)]$

A brown crystalline complex (0.15 g, 0.3 mmol) was dissolved in toluene- d_8 (1.0 mL), and hydrogen (~ 4.2 mmol) was admitted. After stirring overnight at room temperature, the solution color turned more yellow. The solution was further kept at 70 °C for 32 h to give a reddish-ocher solution. Volatiles were distilled under vacuum to a cooled trap and analyzed to contain only 1-phenyl-2-(trimethylsilyl)ethane (for GC-MS and ^1H and ^{13}C NMR data see the ESI †). The residue was **2** (δ_{H} 23.0 ppm).

Hydrogenation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-MeC}\equiv\text{CSiMe}_3)]$

A crystalline complex (0.13 g, 0.3 mmol) was dissolved in toluene- d_8 (1.0 mL), and hydrogen (~ 4.2 mmol) was admitted. After stirring overnight at room temperature, the solution color turned more yellow. Heating to 70 °C for 48 h was required to obtain the reddish-ocher solution of **2** containing propyltrimethylsilane (for ^1H NMR and GC-MS data see the ESI †).

Hydrogenation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$

A solution of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ in toluene- d_8 (0.5 mmol/1.5 mL) after addition of hydrogen remained yellow after 3 days, indicating no visible reaction. Then the solution was heated to 70 °C for 34 h yielding, according to ^1H NMR spectra, **2** (80%) and initial reagent (20%) and olefins. This experiment was repeated with heating to 80 °C for 112 h. The content of the initial reagent was 13% and that of **2** was 87%, and the composition of hydrocarbon products was (*Z*)- $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$ 5%, (*E*)- $\text{Me}_3\text{SiCH}=\text{CHSiMe}_3$ 50%, and $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$ 45% (see the ESI †).

Hydrogenation of $[\text{Cp}^*\text{Ti}(\text{C}_5\text{Me}_3(\text{CH}_2)_2)]$

The doubly tucked-in titanocene crystalline reagent (0.13 g, 0.4 mmol) was dissolved in toluene- d_8 (1.2 mL), and hydrogen (~ 4.2 mmol) was admitted. The blue color of the reagent remained unchanged at room temperature over 24 h, however, after heating to 70 °C for 26 h its color turned ochre. After evaporation of volatiles to dryness the residue was dissolved in

toluene- d_8 and ^1H NMR spectra revealed that the solution contained only **2**.

Hydrogenation of **C1**

Crystalline **C1**²² (0.12 g, 0.25 mmol) in toluene- d_8 (1.2 mL) in the presence of hydrogen (~ 4.2 mmol) did not change its blue color at room temperature overnight. After heating to 70 °C for 26 h its initial blue color turned clear yellow. The volatiles were vacuum-distilled to an NMR tube and the residue was extracted with hexane and crystallized in a freezer by slow distillation off the solvent. The yield of yellow finely crystalline solid was 0.11 g (91%). ^1H and ^{13}C NMR spectra of the product agreed with the data for compound **C2**^{23a} previously obtained by hydrogenation of the acetylenic precursor **C3**^{23b} (Scheme 4). The presence of about 1% amount of 2,7-tetramethyloct-4-ene isomers in the volatiles indicated that the hydrogenation induced also the retrosynthesis of the bicyclic ligand; therefore the further hydrogenation of **C2** at higher temperature was not investigated.

Hydrogenation of $[(\text{C}_5\text{Me}_4\text{tBu})_2\text{Ti}]$

Crystalline titanocene^{12,24} (0.11 g, 0.3 mmol) in toluene- d_8 (1.2 mL) was reacted with hydrogen overnight and the NMR tube was sealed off with a torch under hydrogen. An ochre solution revealed the ^1H NMR spectrum of **5** (see below) and a very broad signal at about 2 ppm attributed to **3**. At -35 °C ^1H and ^{13}C NMR spectra of **3** were resolved and the ^1H NMR spectrum of **5** and the outmost resonance at low magnetic field of $[(\text{C}_5\text{Me}_4\text{tBu})_2\text{Ti}]$ were observed.

Analytical data for compound 3. ^1H NMR (toluene- d_8 , -35 °C): 1.45 (s, 12H, C_5Me_4); 1.48 (s, 18H, CMe_3); 2.10 partly overlapped by a solvent signal (s, 12H, C_5Me_4); 3.04 (s, 2H, Ti-H_2). ^{13}C NMR (toluene- d_8 , -35 °C): 11.56, 16.98 (C_5Me_4); 33.16 (CMe_3); 36.28 (CMe_3); 117.78, 119.01 (C_5Me_4 , C_q); 134.42 (C_5Me_4 , C_{ipso}). The resonance at δ_{H} 2.10 ppm was recognized using a gHMQC experiment.

Hydrogenation of $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}]$

Crystalline titanocene (0.13 g, 0.3 mmol) in toluene- d_8 (1.2 mL) was reacted with hydrogen overnight and the NMR tube was sealed off with a torch under hydrogen. The ^1H NMR spectrum of the ochre solution revealed a very broad signal at 1.6 ppm due to mainly **4**, weak resonances of **6** (see below) and a very broad and extremely weak outmost resonance at low magnetic field of $[\text{Ti}(\text{C}_5\text{Me}_4\text{SiMe}_3)_2]$ (see Fig. S14 in the ESI †). At -35 °C ^1H and ^{13}C NMR spectra of **4** were resolved (see Fig. S15 and S16 in the ESI †), signals of **6** showed a paramagnetic shift and the outmost resonance at low magnetic field of $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}]$ turned narrow and paramagnetically shifted to 99.6 ppm (Fig. 2 and 3). ^1H NMR resonance of dihydrogen at 4.50 ppm was not observed. After degassing by two freezing/thawing cycles the ^1H NMR spectra of the major $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ti}]$ and minor **6** were only observed in a brownish green solution (see Fig. S14 in the ESI †).

Analytical data for compound 4. ^1H NMR (toluene- d_8 , -35 °C): 0.36 (s, 18H, SiMe_3); 1.40, 1.96 ($2 \times$ s, $2 \times$ 12H, C_5Me_4);

2.74 (s, 2H, TiH_2). ^{13}C NMR (toluene- d_8 , -35°C): 2.76 (SiMe_3); 11.23, 15.88 (C_5Me_4); 116.60 (C_5Me_4 , C_{ipso}); 121.72, 125.93 (C_5Me_4 , C_q). Interaction of TiH_2 and SiMe_3 was proved by 1D NOESY.

Hydrogenation of $[(\text{C}_5\text{Me}_4^t\text{Bu})\text{Ti}(\text{C}_5\text{Me}_4\text{CMe}_2\text{CH}_2)]$ to give 5

A crystalline reagent²⁷ (0.4 g, 1.0 mmol) was dissolved in toluene- d_8 (1.0 mL) and hydrogen was admitted to the solution. The initial dark color turned immediately to ochre. After stirring for 30 min the unreacted hydrogen was pumped off and a reddish-ochre solution was investigated by ^1H NMR, EPR and UV-vis spectra. Then, toluene- d_8 was replaced with hexane and the product was crystallized in a refrigerator. Dark red-ochre crystals were recrystallized from hexane and dried under vacuum. Yield 0.33 g, 82%.

Analytical data for compound 5. Mp. 111°C dec. EI-MS (direct inlet, 70 eV, 100°C): m/z (relative abundance) 404 (10), 403 (M^+ ; 36), 402 (68), 401 ($[\text{M} - \text{H}_2]^+$; 89), 400 (60), 399 ($[\text{M} - 2\text{H}_2]^+$; 95), 398 (31), 397 ($[\text{M} - 3\text{H}_2]^+$; 100), 396 (26), 395 ($[\text{M} - 4\text{H}_2]^+$; 43), 394 (19), 393 (41), 381 (26), 346 ($[\text{M} - \text{C}_4\text{H}_9]^+$; 17), 345 (17), 344 ($[\text{M} - \text{H}_2 - \text{C}_4\text{H}_9]^+$; 41), 339 ($[\text{M} - 2\text{H}_2 - \text{C}_4\text{H}_9]^+$; 20), 327 (37), 325 (26), 226 [$\text{M} - \text{Cp}^+$]; (25), 223 (19), 206 (26), 202 (27), 201 (42), 119 (10), 105 (13), 91 (14), 57 (38). IR (KBr, cm^{-1}): 2987 (s, sh), 2954 (vs), 2907 (vs), 2867 (s), 2722 (vw), 1521 (m, b), 1480 (m), 1457 (m, b), 1381 (s), 1373 (s), 1358 (s), 1234 (m), 1200 (w), 1123 (vw), 1038 (w), 1023 (m), 829 (vw), 746 (vw), 712 (vw), 670 (vw), 620 (w), 571 (w), 505 (w), 434 (m). ^1H NMR (toluene- d_8): 3.5 (br s, $\Delta\nu_{1/2} \sim 80$ Hz, 18H, CMe_3); 18.3 (br s, $\Delta\nu_{1/2} \sim 230$ Hz, 12H, C_5Me_4); 22.7 (br s, $\Delta\nu_{1/2} \sim 390$ Hz, 12H, C_5Me_4). EPR (toluene- d_8 , -140°C): $g_{\perp} \sim 1.980$, $g_{\parallel} = 1.776$, $g_{\text{av}} = 1.912$. UV-vis (toluene- d_8 , nm): 310 > 375(sh) \gg 475 > 580 (sh). Found (%): C, 77.35; H, 10.72. $\text{C}_{26}\text{H}_{43}\text{Ti}$ requires (%): C, 77.39; H, 10.74.

Hydrogenation of $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2)]$ to give 6

A crystalline reagent^{24,28} (0.22 g, 0.5 mmol) was hydrogenated in hexane (10 mL). After stirring overnight the initial green color of the solution turned light brown. The unreacted hydrogen was removed under vacuum and the solvent was evaporated to get the saturated solution. Crystallization in a three-necked ampule by slow distillation of the solvent into an arm close to the cooling side of a refrigerator afforded pale brown needle aggregates unsuitable for X-ray investigation. Yield 0.19 g, 87%.

Analytical data for compound 6. Mp. 65°C dec. EI-MS (80°C): m/z (relative abundance) 436 (10), 435 (M^+ ; 36), 434 (68), 433 ($[\text{M} - 2\text{H}]^+$; 100), 432 (26), 431 (15), 361 ($[\text{M} - \text{SiMe}_3\text{H}]^+$; 11), 73 ($[\text{SiMe}_3]^+$; 60), 59 ($[\text{SiMe}_2\text{H}]^+$; 12). IR (KBr, cm^{-1}): 2952 (vs), 2909 (vs), 2865 (s), 2722 (vw), 1525 (m) $\nu(\text{Ti}-\text{H})$, 1480 (w), 1448 (m), 1404 (w), 1378 (s), 1348 (w), 1329 (m), 1245 (s), 1128 (w), 1083 (vw), 1022 (m), 992 (vw), 948 (vw), 846 (vs), 782 (m), 756 (m), 687 (m), 669 (w), 633 (m), 576 (w), 511 (w), 469 (m), 429 (m). Upon exposure of the KBr pellet to air the absorption band at 1525 cm^{-1} disappeared and new bands at 780 and 577 cm^{-1} grew strong in intensity. ^1H NMR (toluene- d_8): 2.0 (br s, $\Delta\nu_{1/2} \sim 50$ Hz, 18H, SiMe_3); 13.7 (br s, $\Delta\nu_{1/2} \sim 150$ Hz,

12H, C_5Me_4); 27.9 (br s, $\Delta\nu_{1/2} \sim 290$ Hz, 12H, C_5Me_4). EPR (toluene- d_8 , -160°C): $g_{\perp} = 1.980$, $g_{\parallel} = 1.808$, $g_{\text{av}} = 1.922$. UV-vis (toluene- d_8 , nm): 318 > 375(sh) \gg 470 > 580(sh). Found (%): C, 66.12; H, 9.92. $\text{C}_{24}\text{H}_{43}\text{Si}_2\text{Ti}$ requires (%): C, 66.17; H, 9.95.

Reaction of 5 with butadiene to give 7

Crystalline hydride (0.23 g, 0.6 mmol) was dissolved in hexane (3.0 mL) and butadiene (~ 0.2 mL, >2 mmol) was added. After 30 min at room temperature all volatiles were evaporated under vacuum and a brown residue was dissolved in hexane and crystallized by slow solvent distillation in a refrigerator. A brown finely crystalline powder was obtained after separation of *ca.* 0.2 mL of mother liquor. The product was recrystallized from hexane at -28°C in a freezer. Yield 0.23 g, 85%.

Analytical data for compound 7. Mp. 103°C dec. EI-MS (direct inlet, 70 eV, 100°C): m/z (relative abundance) 457 (M^+ not observed), 404 (22), 403 (57), 402 ($[\text{M} - \text{C}_4\text{H}_7]^+$; 100), 401 (65), 400 ($[\text{M} - \text{C}_4\text{H}_7 - \text{H}_2]^+$; 63), 399 (67), 398 (25), 397 (57), 396 (15), 345 (16), 344 ($[\text{M} - \text{C}_4\text{H}_7 - \text{C}_4\text{H}_{10}]^+$; 41), 343 (14), 341 (13), 339 (25), 327 (37), 325 (22), 226 (25), 223 (14), 206 (26), 202 (27), 201 (37), 187 (18), 119 (10), 105 (13), 91 (14), 57 (68), 55 (48), 43 (40), 41 (73), 39 (29). IR (KBr, cm^{-1}): 2991 (s), 2953 (vs), 2906 (vs), 2867 (s, sh), 2722 (vw), 1629 (w), 1455 (s, b), 1380 (s), 1358 (vs), 1234 (s), 1198 (m), 1150 (w), 1122 (m), 1063 (w), 1035 (m), 1022 (s), 975 (w), 958 (m), 866 (vw), 836 (vw), 818 (vw), 761 (vw), 711 (vw), 664 (w), 642 (w), 618 (m), 572 (w), 492 (w), 473 (w), 453 (vw), 423 (s). EPR (toluene- d_8 , 22°C): $g_{\text{iso}} = 1.956$, $\Delta H = 38$ G; (toluene- d_8 , -140°C): $g_1 = 1.997$, $g_2 = 1.985$, $g_3 = 1.895$, $g_{\text{av}} = 1.959$. UV-vis (toluene- d_8 , nm): 380(sh) \gg 500 > 605(sh). The ^1H NMR spectrum attributed to 7 is shown in Fig. S21 in the ESI.† Found: C, 77.77; H, 10.81. $\text{C}_{30}\text{H}_{49}\text{Ti}$ requires (%): C, 78.74; H, 10.79.

Reaction of 6 with butadiene to give 8

A crystalline reagent (0.20 g, 0.46 mmol) was dissolved in hexane (3.0 mL) and butadiene (~ 0.2 mL, >2 mmol) was added. After 30 min at room temperature all volatiles were evaporated under vacuum and a brown residue was dissolved in hexane and crystallized by a slow solvent distillation in a refrigerator. A brown finely crystalline powder was obtained after separation of *ca.* 0.2 mL of mother liquor. Recrystallization from the same hexane afforded pale greenish-brown crystals. Yield 0.19 g, 84%.

Analytical data for compound 8. EI-MS (130°C): m/z (relative abundance) 489 (M^+ ; 3), 474 ($[\text{M} - \text{Me}]^+$; 6), 437 (19), 436 (65), 435 (70), 434 (83), 433 ($[\text{M} - \text{C}_4\text{H}_8]^+$; 100), 432 (81), 431 (9), 430 (12), 429 (14), 419 (12), 418 ($[\text{M} - \text{C}_4\text{H}_8 - \text{Me}]^+$; 21), 362 (12), 361 (31), 360 ($[\text{M} - \text{C}_4\text{H}_8 - \text{Me} - \text{SiMe}_3]^+$; 30), 359 (20), 358 (11), 287 ($[\text{M} - \text{C}_4\text{H}_8 - \text{Me} - 2\text{SiMe}_3]^+$; 17), 285 (13), 217 (16), 208 (18), 73 (87), 59 (17), 57 (13), 56 (48), 55 (39), 45 (21). IR (KBr, cm^{-1}): 3015 (w), 2970 (s, sh), 2950 (s), 2908 (s, b), 2850 (m, sh), 2720 (vw), 1629 (w), 1480 (w), 1450 (m), 1432 (w), 1416 (w), 1407 (w), 1378 (m), 1347 (m), 1246 (vs), 1146 (w), 1127 (m), 1059 (w), 1020 (m), 982 (vw), 953 (w), 847 (vs), 835 (vs), 755 (s), 686 (m), 659 (w), 634 (m), 576 (vw), 417 (m). The band at 576 cm^{-1} grew in intensity upon exposure of the KBr

pellet to air. EPR (toluene- d_8 , 22 °C): $g_{\text{iso}} = 1.962$, $\Delta H = 24$ G; (toluene- d_8 , -140 °C): $g_1 = 2.000$, $g_2 = 1.985$, $g_3 = 1.901$, $g_{\text{av}} = 1.962$ (impurity Cp'2Ti-OR: $g_{\text{iso}} = 1.976$, $\Delta H = 3.5$ G, $a_{\text{Ti}} = 7.8$ G; (-140 °C): $g_1 = 2.000$, $g_2 = 1.983$, $g_3 = 1.953$, $g_{\text{av}} = 1.978$). UV-vis (toluene- d_8 , nm): 485 > 620(sh). ^1H NMR spectrum of **8** showed mainly very broad signals (6000–10 000 Hz) centered at *ca.* 8–12 ppm (see Fig. S22 in the ESI†). Found (%): C, 68.64; H, 9.97. $\text{C}_{28}\text{H}_{49}\text{Si}_2\text{Ti}$ requires (%): C, 68.67; H, 10.01.

Attempted reaction of titanocenes [(C₅Me₄tBu)₂Ti] and [(C₅Me₄SiMe₃)₂Ti] with butadiene

Solutions from the above described hydrogenation of titanocenes [(C₅Me₄tBu)₂Ti] and [(C₅Me₄SiMe₃)₂Ti] yielding equilibria with their dihydrides and showing the monohydrides **5** and **6** as impurities were degassed by two freezing/thawing cycles and *ca.* 0.2 mL of liquid butadiene was added to each solution afterwards. After standing for one day at room temperature all volatiles were evaporated to dryness and the residues were dissolved in toluene- d_8 . Both samples revealed the ^1H NMR spectra of titanocenes and 2-buten-1-yl derivatives **7** and **8** (see Fig. S21 and S22 in the ESI†) whereas the volatiles contained unreacted butadiene. The inertness of these titanocenes towards butadiene was thus proved.

X-ray crystallography

Suitable samples of **1A** (CCDC 1545965), **1B** (CCDC 1545966), **5** (CCDC 1545967), and **8** (CCDC 1545964) were filled into Lindemann glass capillaries under a purified argon atmosphere in a Labmaster 130 glovebox (mBraun). Diffraction data were collected using MoK α radiation ($\lambda = 0.71073$ Å) either on a Nonius Kappa diffractometer equipped with a Bruker ApexII-CCD detector (**5**, **8**) or on a Bruker D8 Venture diffractometer (**1A**, **1B**). For the measurement of crystal samples having larger dimensions, a diffractometer employing a 0.6 mm collimator and no focussing of the primary beam was employed. The phase problem was solved by intrinsic phasing (SHELXT)⁴⁰ and the structure models were refined by full matrix least squares on F^2 (SHELXL-2014).⁴⁰ All non-hydrogen atoms were refined anisotropically. Unless otherwise given, hydrogen atoms were placed in idealized positions and refined isotropically using the riding model. Molecular graphics was carried out using PLATON.⁴¹

In the solid-state structure of **1A**, apart from the dihydride complex its parent monochloride analogue occupied the same position in the unit cell. The two hydrogen atoms bonded to titanium were refined with coordinates left free to vary and with site occupation factors constrained with that of the chloride atom. The site occupation factors were constrained to yield one after summing; their final values became 0.32 for the chloride and 0.68 for both hydride atoms. In addition to this disorder on the bent titanocene complex, the asymmetric part of the unit cell included an additional one-half of a permethyl-titanocene molecule, whose heavy atoms were refined with no constraints, while its hydrogen atoms were refined only isotropically and using the riding model. In the case of **1B** there were two symmetrically independent molecules present in the

asymmetric part of the unit cell; however, both molecules were struck with a similar disorder (with the monochloride analogue present) as for **1A**. The treatment of the disorder was analogous with the former case.

For complex **5** there were two symmetrically independent molecules present in the asymmetric part of the unit cell. One of the two molecules had, together with the monohydride complex discernible on the Fourier maps, the analogous oxo-complex also. The refinement of this disorder was done by constraining the respective site occupation factors. In complex **8**, the disorder of the aliphatic ligand overlapping with a chloride was treated analogously with the above cases.

Computational details

DFT calculations were carried out at the Fermi cluster at the J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, v.v.i. using Gaussian 09, Revision D.01.⁴² Geometry optimizations and NBO analyses were done using the M06 functional and the 6-31G(d,p) basis set used for all atoms. The Hessians were computed analytically before starting the first geometry optimization steps. All calculations were performed using ultrafine integration grids.

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