ORGANOMETALLICS

Ethene Elimination during Thermolysis of Bis(3-butenyltetramethylcyclopentadienyl)dimethyltitanium

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Supporting Information

ABSTRACT: Thermolysis of $[TiMe_2\{\eta^5-C_5Me_4(CH_2CH_2CH=CH_2)\}_2]$ (1) in toluene at 120 °C for 4 h resulted in the formation of the cyclopentadiene ringtethered titanacyclobutane $[Ti^{IV}{\eta^5-C_5Me_4CH_2CH_2CH(\kappa-CH)}_2CH_2]$ (2) in virtually quantitative yields. Thermolysis in an NMR tube at 100 °C revealed that initial elimination of methane is followed by addition of one 3-butenyl double bond to a titanocene-methylidene moiety. The formed titanacyclobutane intermediate $[Ti{\eta^{5}-C_{5}Me_{4}(CH_{2}CH_{2}CH=CH_{2})}{\eta^{5}-C_{5}Me_{4}CH_{2}CH_{2}CH(\kappa-CH)CH_{2}CH_{2}-CH_{2}CH_{$ $(\kappa$ -CH₂)] (4) then underwent a metathesis reaction with the pendant 3-butenyl to



give 2 and free ethene. Cleavage of Ti-C bonds of 2 with HCl afforded stable ansa-[TiCl₂{ η^{5} -C₅Me₄(CH₂)₇ η^{5} -C₅Me₄}] (3). Sunlight photolysis of 1 gave rise to the cyclopentadiene ring-tethered titanacyclopentane $[Ti^{IV}{\eta^5-C_5Me_4(CH_2CH_2CH(\kappa-1))}]$ CH)CH₂ $_{2}$ (5), the known product of cycloaddition reactions following the removal of chlorine atoms from [TiCl₂ η^{5} - $C_5Me_4(CH_2CH_2CH=CH_2)_2$ with magnesium (as found by Horaček, M. et al. Chem. Eur. J. 2000, 6, 2397).

INTRODUCTION

It has been shown that reduction of group 4 metallocene dichlorides bearing pendant ω -alkenyl groups on their cyclopentadienyl ligands induce the formal [2 + 2 + 2] cycloaddition reaction of two d electrons of transient metallocene (M^{II}) and two pairs of double-bond π electrons.¹ Independently of the metal (Ti, Zr, and Hf), the cycloaddition generates cyclopentadienyl ring tethered metallacyclopentanes according to Scheme 1. For titanocenes, the sterically convenient structure contains dimethylene tethers as consistent with 3-butenyl pendant groups yielding compound 5; for longer alkenyl chains, e.g. 4-pentenyl, the double bonds are shifted into internal positions to give rise to a 3,4-dimethyl-substituted titanacyclopentane moiety.^{1a} The key metallocene transient species were obtained from metallocene dichlorides by reductive chlorine abstraction with magnesium (for Ti)^{1a,b} or sodium amalgam (for Zr and Hf)^{1c} or by chloride metathesis with LiBu (for Zr) followed by butyl elimination.^{1d} With regard to the latter method, the formation of d² metallocene complexes with olefins arising from alkyl disproportionation has been exploited in the synthesis of numerous metallacyclopentene and metallacyclopentadiene complexes, where π -coordinated olefins took part in cycloaddition reactions with free alkenes or alkynes.² In contrast with the latter systems, the above d² complexes with pendant double bonds neither afford products with olefins generated from alkyl disproportionation^{1d} nor do they coordinate bis(trimethylsilyl)acetylene added to the system.^{1a,b} Thus, products arising from activation of pendant double bonds can afford valuable information on the structure of activating metal species. In this respect, products of thermolysis

and photolysis of the well-defined bis(3-butenyltetramethylcyclopentadienyl)dimethyltitanium, [TiMe₂{ η^{5} -C₅Me₄(CH₂CH₂- $CH=CH_2$] (1),³ are of interest. This compound melts without decomposition at 72 °C;³ however, its thermolysis might occur at about 110 °C, the temperature at which the parent compound of the persubstituted titanocene series $[TiMe_2Cp_2^*]$ $(Cp^* = \eta^5 - C_5 Me_5)$ releases the first Me group to give methane and the singly tucked-in methyltitanocene $[TiMe(Cp^*){C_5Me_4}]$ (CH_2)].^{43,b'} The thorough study of this reaction using the deuterated compounds [Ti(CD₃)₂Cp*₂] and [TiMe₂(Cp* d_{15}] gave evidence that the methane evolved was formed from the rupture of one Ti-Me bond followed by hydrogen transfer from the other Ti-Me bond. This led to the formation of the titanocene-methylidene intermediate $[Ti(=CH_2)Cp_2^*]$, which consequently rapidly rearranged to the singly tucked-in compound (Scheme 2). The Cp* ligands were shown not to interfere with methane elimination.^{4c} Since the analogous methane elimination from $[TiMe_2(\eta^5-C_5Me_4R)_2]$ (R = ^{*T*}Bu, CH₂Ph) compounds also proceeds at 110 °C,^{4d} the thermolysis of 1 should occur at about the same temperature without interference with the 3-butenyl substituents.

On the other hand, the photolysis of dimethyltitanocene, $[TiMe_2Cp_2]$, has been studied extensively; however, it is not yet fully understood. It was assumed that photolytically formed methyl radicals abstract hydrogen from hydrocarbon solvents to yield methane, and some thermally stable, insoluble form of

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Scheme 1



Scheme 2



titanocene was obtained. The presence of a titanocene species in the latter product was proved by its reaction with tolane, PhC==CPh, which gave bis(cyclopentadienyl)titanatetrapheny-lcyclopentadiene, albeit in yields up to 50%.⁵ This compound was cleanly obtained from the reaction of tolane with titanocene at the onset of its formation during the reduction of [TiCl₂Cp₂] with magnesium^{6a} or with the well-defined titanocene –bis(trimethylsilyl)ethyne complex.^{6b} The titanocene dimethyls [TiMe₂Cp''₂] (Cp'' = η^{5} -C₅Me₅, C₅Me₄SiMe₃, C₅Me₄^tBu) are also sensitive to sunlight, however, with a photolytic efficiency apparently lower than for [TiMe₂Cp₂].^{4c,7}

Here, we report on thermolytic products of 1, a metathetic mechanism of the final product formation, and the result of photolysis of 1 with sunlight.

RESULTS AND DISCUSSION

Heating of 1 in toluene to 120 °C for 4 h afforded cleanly the red crystalline solid 2 (eq 1), whose EI-MS spectrum showed the molecular ion at m/z 384 to be the base peak, undergoing only negligible fragmentation. The molecular ion thus indicated that one molecule of methane and one molecule of ethene were liberated during thermolysis to give a thermally robust 2.



Compound 2 did not yield crystals suitable for X-ray diffraction analysis; however, its structure was unequivocally determined by ¹H and ¹³C NMR spectroscopy using quantitative ¹³C NMR, gHSQC, gHMBC, and COSY experiments. The spectral assignment is consistent with the C_2 symmetry of the molecule, the rotation axis passing through the titanium atom and methylene carbon atom of the titanacyclobutane ring. The titanacyclobutane ring is characterized by the high-field-shifted ¹H and ¹³C resonances of the methylene unit ($\delta_{\rm H}$ –0.05 ppm; $\delta_{\rm C}$ 11.9 ppm)



Figure 1. Computed molecule of 2 containing a 2-fold axis passing through titanium and methylene carbon atoms. Hydrogen atoms are not visualized for clarity. Geometric parameters within the titanacyclobutane moiety are as follows: Ti-C = 2.15 Å, C-C = 1.57 Å, $C-Ti-C = 76.28^{\circ}$, $Ti-C-C = 84.31^{\circ}$, $C-C-C = 115.09^{\circ}$.

that is common for titanacyclobutane compounds.^{8a} These chemical shifts were found to be only slightly dependent on substituents at the C_{α} atoms^{8b} and the cyclopentadienyl ligand substituents.^{8c} The methine *CH* groups σ -bonded to titanium displayed signals at $\delta_{\rm H}$ 2.70–2.80 ppm and $\delta_{\rm C}$ 95.7 ppm, values close to those found for Ti*CH* in the cyclopentadienyl ring tethered titanacyclopentanes (78.4–86.2 ppm).^{1a} Four singlet signals for nonequivalent methyl groups were resolved for cyclopentadienyl ligands ($\delta_{\rm H}$ 1.63, 1.73, 1.75, 1.76 ppm; $\delta_{\rm C}$ 10.9, 11.2, 12.4, 12.7 ppm). The molecule rigidity gave rise to diastereotopic protons in the CH₂CH₂ tether (C₅CH₂, $\delta_{\rm H}$ 2.20, 2.33 ppm; C₅CH₂CH₂, $\delta_{\rm H}$ 2.83, 2.98 ppm).

The structure of **2** was also constructed using the usual bond lengths and valence angles and optimized by DFT calculations to give a slightly asymmetrical molecule. In order to calculate ¹H and ¹³C NMR spectra, the molecular structure was symmetrized by imposing a 2-fold rotation axis, whose presence was derived from the experimental NMR data. The optimized symmetrical structure (Figure 1) did not lead to an increase of the total energy of the molecule, and calculated Ti–C bond lengths and valence angles within the titanacyclobutane ring fell into the range of crystal structure parameters known for three bis(cyclopentadienyl)titanacyclobutane derivatives.^{8a} The chemical shifts computed on this symmetrical molecule were in excellent agreement with experimental data (see the Supporting Information).

Compound 2 appeared to be inert toward oxidative chlorination with $PbCl_2$ in THF;⁹ however, its Ti–C bonds were cleanly cleaved with anhydrous $HCl^{1a,b}$ to give the corresponding *ansa*titanocene dichloride containing the heptamethylene bridging chain, 3 (eq 2).



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Scheme 3



Compound 3 did not give single crystals for X-ray diffraction analysis; however, its ¹H and ¹³C NMR spectra allowed a full assignment using a combination of 1D TOCSY, gHSQC, and gHMBC experiments. The average $C_{2\nu}$ symmetry of 3 gave rise to two signals for methyl groups of cyclopentadienyl ligands ($\delta_{
m H}$ 1.98, 2.00 ppm; $\delta_{\rm C}$ 13.8, 14.7 ppm) and one downfield-shifted multiplet centered at $\delta_{\rm H}$ 2.25 ppm and corresponding $\delta_{\rm C}$ 24.8 ppm attributable to a methylene group (α -CH₂) attached to the cyclopentadienyl ring. The remaining methylene units of the ansa bridge displayed an unresolved multiplet at $\delta_{\rm H}$ 1.28–1.56 ppm in the ¹H NMR spectrum and distinct signals in ¹³C NMR spectrum for aliphatic CH₂ groups (δ -CH₂, δ _C 20.2 ppm; β -CH₂, $\delta_{\rm C}$ 25.9 ppm; γ -CH₂, $\delta_{\rm C}$ 28.0 ppm).The EI-MS spectra of 3 displayed a low-abundant molecular ion at m/z 456, whereas the fragment $[M - Cl]^+$ was the base peak. The next fragment ion at m/z 217 ([M - Cl - C₅Me₄(CH₂)₆]⁺) of low-tomedium abundance is also consistent with the composition of 3. In the infrared spectrum, the absorption band at 750 cm^{-1} is indicative of the heptamethylene chain.

Insight into the mechanism of formation of **2** was obtained from ¹H and ¹³C NMR spectra of the thermolysis of **1** at 100 °C in C_6D_6 in a flame-sealed NMR sample tube. The initial overwhelming reaction was the liberation of methane, resulting in the formation of an intermediate product (4) which, in a successive reaction, yielded **2** with evolution of ethene (Scheme 3). The product mixture **1** (14%), **2** (20%), and **4** (66%) with a maximum yield of **4** was obtained after 10 h. This composition did not change upon keeping the NMR sample tube at room temperature for 1 week, suggesting that **4** is a stable intermediate. Further heating of the mixture at 100 °C for 35 h afforded virtually pure **2** and roughly equal amounts of evolved ethene and methane (see the Supporting Information).

The structure of 4 as depicted in Scheme 3 was determined from ¹H and ¹³C NMR spectra of the reaction mixture above containing the maximum yield of 4. The molecule possesses a titanacyclobutane ring tethered at its C_{α} atom with a dimethylene spacer to one cyclopentadienyl ring (Ti*CH*, $\delta_{\rm H}$ 2.32–2.40 ppm, $\delta_{\rm C}$ 96.32 ppm), a feature known for **2**. The presence of one methylene group linked to the titanium atom was deduced from signals at $\delta_{\rm H}$ 1.88–1.97 and 2.08–2.16 ppm and $\delta_{\rm C}$ 73.9 ppm, and the presence of a distant titanacyclobutane methylene group was indicated by strongly high-field-shifted resonances at $\delta_{\rm H}$ –0.68 to –0.52 and 0.23–0.38 ppm and $\delta_{\rm C}$ 1.9 ppm, which are typical of known titanacyclobutanes.⁸ The remaining pendant butenyl group in 4 gave $\delta_{\rm H}$ and $\delta_{\rm C}$ chemical shifts almost identical with those for 1. The absence of molecular symmetry gave rise to eight singlet signals for cyclopentadienyl methyl groups in ¹H ($\delta_{\rm H}$ 1.50, 1.70, 1.72, 1.73, 1.74, 1.76, 1.78, 1.84 ppm) and seven signals in ¹³C NMR spectra ($\delta_{\rm C}$ 10.62, 10.64, 11.52, 11.59, 11.63, 11.79 (2C), 12.02 ppm).

These observations allowed us to formulate the thermally induced conversion of 1 to 2 as a multistep process (see Scheme 3). In the first step, the initiating elimination of methane from 1 is followed by addition of one pendant double bond to the postulated titanocene-methylidene species $[Ti(=CH_2)Cp'_2]$ $(Cp' = \eta^5-C_5Me_4CH_2CH_2CH=CH_2)$ to give the cyclopentadienyl ring tethered titanacyclobutane intermediate 4. Compound 4 was shown to be thermally stable at ambient temperature on a time scale of days; however, at 100 °C it was concurrently eliminating ethene while coordinating the second pendant double bond. Its cycloaddition to a titanium-propylidene species afforded the thermally robust product 2.

Most of the reactions of Scheme 3 have their counterparts in the degenerate metathesis chemistry of the titanocene-methylidene species [Ti(=CH₂)Cp₂]¹⁰ stabilized by coordination to dialkylaluminum chlorides as the Tebbe reagent $[Cp_2TiCH_2(\mu-Cl)-$ AlMe₂].¹¹ Tebbe reagent stability, however, has been shown to decrease with increasing electron density on the titanium atom induced by substitution of the cyclopentadienyl rings with methyl groups. Tebbe reagents have thus only been prepared for titanocenes with a limited number of methyl substituents: e.g., Ti- $(C_5H_4Me)_2$ and $Ti(1,2,4-C_5H_2Me_3)(C_5H_5)$.^{8c} For the [Ti- $(=CH_2)Cp_2^*$ species, the thermolysis of $[TiMe_2Cp_2^*]$ is apparently the only source,¹² albeit not suitable for its exploitation in addition reactions. Our experiments performed in an NMR tube showed that thermolysis of $[TiMe_2Cp_2^*]$ in the presence of excess tolane at 110 °C did not afford either diphenyltitanacyclobutene or tolane insertion products into Ti-Me bond(s), the only product being the singly tucked-in $[TiMe(Cp^*){C_5Me_4(CH_2)}]$. The $[Ti(=CH_2)Cp_2^*]$ species was only partially trapped when $[TiMe_2Cp_2^*]$ was thermolyzed in the presence of organic epoxides to give decamethyltitanocene enolates.¹³

In contrast, the conversion of 1 to 4 implies that the analogous titanocene–methylidene intermediate $[Ti(=CH_2)Cp'_2]$ reacts

easily with the 3-butenyl double bond. The mode of its addition to the $Ti=CH_2$ bond results in linking the dimethylene tether exclusively to C_{α} of titanacyclobutane, the arrangement that was proved to be sterically convenient for the cyclopentadienyl ring tethered titanacyclopentanes.^{1a} For nontethered titanacyclobutanes both C_{α} - and C_{β} -monosubstituted derivatives are known. Addition of the bulky monosubstituted alkenes tert-butylethene and styrene to $[Ti(=CH_2)Cp_2]$ gave C_β -substituted titanacyclobutanes;⁸ however, the phenyl group shift to C_{α} was induced thermally at room temperature only.^{8b} This rearrangement was suggested to occur for sterically reasons; however, more sterically congested decamethyltitanocene titanacyclobutanes substituted at C_{β} were not reported to isomerize.¹⁴ No sterically induced rearrangements were observed for the permethyltitanocene titanacyclobutane with an exo methylene substituent on C_{α} decomposing only at 170 °C,^{15a} and for its highly thermally stable analogous titanacyclobutenes bearing even bulky Ph and SiMe₃ substituents on the ring double bond.^{15b}

The following ethene elimination from 4 is a productive metathesis step which was previously observed only in the equilibrium reaction of transient $[Ti(=CH_2)Cp_2]$ with 1,1-disubstituted allenes.¹⁶ Here, the process of ethene replacement with the second pendant double bond is to be facilitated by a much higher encounter frequency of the pendant double bond in the ligand field of titanium compared to that of free ethene. Since approximate theoretical calculations found a small energy difference for the model Ti(IV) titanacyclobutane and Ti(II) titanocene—methylidene with π -coordinated ethene, ^{10d,17} the completion of conversion of 1 to 2 is due to the high stability of the titanacyclobutane moiety fixed at the open side of the titanocene shell by two dimethylene tethers (Figure 1).

Exposure of a toluene solution of 1 to sunlight for 3 weeks resulted in isolation of a red crystalline product in about 40% yield. The X-ray diffraction analysis of single crystals as well as successive ¹H and ¹³C NMR spectra showed that it is the cyclopentadienyl ring tethered titanacyclopentane 5 (depicted in Scheme 1). This indicates that the photolysis of 1 generates a persubstituted titanocene species capable of reacting with the pendant double bonds in a manner known for the chemical reduction induced cycloaddition reaction.^{1a} The mother liquor contained, according to ¹H NMR spectra and EI-MS spectra, a variety of products containing compound 1 as the main component. Photolysis of 1 with sunlight was not further investigated because of the low efficiency and low selectivity of the product formation.

CONCLUSIONS

Thermolysis of 1 revealed that transiently formed titanocenemethylidene reacts with one pendant double bond with unprecedented efficiency to give the cyclopentadienyl ring tethered titanacyclobutane 4. In contrast to nontethered titanacyclobutanes, which generally undergo nonproductive (degenerate) metathesis with olefins,¹⁸ compound 4 eliminates ethene while forming doubly cyclopentadienyl ring tethered titanacyclobutane 2 in a productive metathesis step. The reason for the high selectivity and full conversion of 1 to 2 is to be sought in the circumstance that the whole process proceeds in the ligand field of the central titanium atom and in the high stability of 2. The substantial photolytic conversion of 1 to 5 indicates the formation of a titanocene species, as previously assumed for simple titanocene dimethyl photolysis.⁵

EXPERIMENTAL SECTION

General Considerations. Degassed solutions of 1 were handled on a vacuum line in sealed all-glass devices equipped with breakable seals. ¹H (300 and 500 MHz) and ¹³C (75 and 125 MHz) NMR spectra were recorded on a Varian Mercury 300 and Varian INOVA 500 spectrometers in C₆D₆ solutions at 25 °C. Chemical shifts (δ /ppm) are given relative to solvent signals (C₆D₆: $\delta_{\rm H}$ 7.15 ppm, $\delta_{\rm C}$ 128.00 ppm). EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into a direct-inlet probe under argon. IR spectra of samples in KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400-4000 cm⁻¹. KBr pellets were prepared in a Labmaster 130 glovebox (mBraun) under purified nitrogen. Photolysis experiments were performed in the summer with sunlight that passed through two 2.5 mm glass windows and the 2 mm Pyrex glass of the ampule. Elemental analyses were carried out on a Flash EA2000 CHN/O automatic elemental analyzer (Thermo Scientific).

Chemicals. The solvents tetrahydrofuran (THF), hexane, toluene, benzene- d_{6_0} and toluene- d_8 were dried by refluxing over LiAlH₄ and stored as solutions of the dimeric titanocene $[(\mu \cdot \eta^5 \cdot \Gamma_5 H_4 C_5 H_4)(\mu \cdot H)_2 \{\text{Ti}(\eta^5 \cdot C_5 H_5)\}_2]^{19}$ The titanocene dimethyl species $[\text{TiMe}_2 \{\eta^5 \cdot C_5 Me_4 (CH_2 CH_2 CH=CH_2)\}_2]$ (1) was prepared from $[\text{TiCl}_2 \{\eta^5 \cdot C_5 Me_4 (CH_2 CH_2 CH=CH_2)\}_2]^{1a}$ by reaction with LiMe in diethyl ether under argon and characterized by ¹H and ¹³C NMR, EI-MS, and IR (KBr) data in full agreement with reported data.³ $[\text{TiMe}_2 Cp^*_2]$ was obtained analogously.^{2b} PbCl₂ and PhC=CPh (both Aldrich) were weighed and degassed. Gaseous HCl was made from NaCl by adding degassed H₂SO₄ (98%) in an ampule on a vacuum line.

Preparation of [Ti{ η^5 -C₅Me₄(CH₂CH₂CH(*κ*-CH)}₂CH₂] (2). Compound 1 (0.30 g, 0.70 mmol) was dissolved in toluene (10 mL), and the solution was heated to 120 °C for 4 h in a sealed ampule. The orange solution changed to dark red. The ampule was opened on a vacuum line at ambient temperature, all volatiles were evaporated under vacuum, and the brownish red residue was dissolved in 2 mL of hexane. The solution was concentrated to crystallization by a slow distillation of hexane into a cooler ampule arm in a refrigerator. A few drops of brown mother liquor were separated from the red crystalline solid of **2**. Recrystallization from hexane at -28 °C afforded crystalline product not suitable for X-ray diffraction analysis. Yield: 0.23 g (86%).

Data for 2 are as follows. Mp: 170 °C. EI-MS (150 °C): m/z (relative abundance, %) 386 (15), 385 (39), 384 (M^{.+}; 100), 383 (16), 382 (17), 341 (8), 339 (8), 182 (7), 181 (10), 180 (8), 178 (10). ¹H NMR (C_6D_6) : -0.05 (dd, ${}^{3}J_{HH}$ = 9.6 Hz, ${}^{3}J_{HH}$ = 7.5 Hz, 2H, CHCH₂CH); 1.63, 1.73, 1.75, 1.76 (4 × s, 4 × 6H, C_5Me_4); 2.20 (ddd, ² $J_{\rm HH}$ = 13.8 Hz, ${}^{3}J_{\rm HH} = 9.9$ Hz, ${}^{3}J_{\rm HH} = 7.5$ Hz, 2H, C₅CH₂CH₂, H^a); 2.33 (ddd, ${}^{2}J_{\rm HH} =$ 13.8 Hz, ${}^{3}J_{HH} = 8.4$ Hz, ${}^{3}J_{HH} = 3.0$ Hz, 2H, C₅CH₂CH₂, H^b); 2.70–2.80 (m, 2H, TiCH); 2.79–2.87 (m, 2H, $C_5CH_2CH_2$, H^a); 2.91–3.05 (m, 2H, $C_5CH_2CH_2$, H^b). ¹³C{¹H} NMR (C_6D_6): 10.85, 11.18, 12.43, 12.70 (C₅Me₄); 11.87 (CHCH₂CH); 24.11 (C₅CH₂CH₂); 49.07 (C₅CH₂CH₂); 95.66 (TiCH); 109.79, 111.69, 114.17, 119.46 (C_a) C_5 Me₄); 134.18 (C_{ipso}). gCOSY (C_6D_6): ¹H/¹H -0.05/2.70-2.80 (CHCH₂CH/TiCH); 2.20/2.33, 2.79–2.87, 2.91–3.05 (C₅CH₂CH₂ $(H^{a})/C_{5}CH_{2}CH_{2}$ (H^{b}) , $C_{5}CH_{2}CH_{2}$ (H^{a}) , $C_{5}CH_{2}CH_{2}$ (H^{b}) ; 2.33/ 2.20, 2.79–2.87, 2.91–3.05 $(C_5CH_2CH_2 (H^b)/C_5CH_2CH_2 (H^a))$ $C_5CH_2CH_2$ (H^a), $C_5CH_2CH_2$ (H^b)); 2.70-2.80/-0.05, 2.91-3.05 $(TiCH/CHCH_2CH, C_5CH_2CH_2 (H^b)); 2.79-2.87/2.20, 2.33,$ 2.91-3.05 ($C_5CH_2CH_2$ (H^a)/ $C_5CH_2CH_2$ (H^a), $C_5CH_2CH_2$ (H^b), C₅CH₂CH₂ (H^b)); 2.91-3.05/2.20, 2.33, 2.70-2.80, 2.79-2.87 $(C_5CH_2CH_2 (H^b)/C_5CH_2CH_2 (H^a), C_5CH_2CH_2 (H^b), CHCH_2CH,$ $C_5CH_2CH_2$ (H^a)). gHSQC (C_6D_6): ${}^{1}H/{}^{13}C$ -0.05/11.87 (CHCH₂-CH/CHCH₂CH); 1.63/10.85, 1.73/11.18, 1.75/12.70, 1.76/12.43 (C_5Me_4/C_5Me_4) ; 2.20, 2.33/24.11 $(C_5CH_2CH_2 (H^a), C_5CH_2CH_2$ $(H^{b})/C_{5}CH_{2}CH_{2}$; 2.75/95.66 (TiCH/TiCH); 2.83, 2.98/49.07 $\begin{array}{l} (C_5 CH_2 CH_2 \ (H^a), \ C_5 CH_2 CH_2 \ (H^b)/C_5 CH_2 CH_2). \ gHMBC \ (C_6 D_6): \\ {}^{1}H/{}^{13}C \ (selected \ signals) \ -0.05/49.07, \ 95.66 \ (CHCH_2 CH/C_5 CH_2 CH_2, TiCH); \ 2.20, \ 2.33/49.07, \ 95.66, \ 111.69, \ 119.46, \ 134.18 \ (C_5 CH_2 CH_2 \ (H^a), \ C_5 CH_2 CH_2 \ (H^b)/C_5 CH_2 CH_2, \ TiCH, \ C_5 Me_4, \ C_5 Me_4, \ C_{ipso}); \ 2.91-3.05/11.87, \ 24.11, \ 95.66 \ (C_5 CH_2 CH_2 \ (H^b)/CHCH_2 CH, \ C_5 CH_2 \ CH_2, \ TiCH). \ IR \ (KBr, \ cm^{-1}): \ 2966 \ (s, \ sh), \ 2940 \ (s, \ sh), \ 2903 \ (vs), \ 2853 \ (s), \ 2805 \ (s), \ 2719 \ (w), \ 1449 \ (m), \ 1439 \ (s), \ 1375 \ (s), \ 1326 \ (w), \ 1306 \ (m), \ 1220 \ (w), \ 1188 \ (vw), \ 1143 \ (vw), \ 1086 \ (vw), \ 1022 \ (m), \ 907 \ (vw), \ 790 \ (vw), \ 672 \ (vw), \ 533 \ (w), \ 464 \ (w), \ 456 \ (w), \ 420 \ (s). \ Anal. \ Calcd \ for \ C_{25}H_{36}Ti \ (384.44): \ C, \ 78.11; \ H, \ 9.44. \ Found: \ C, \ 78.18; \ H, \ 9.47. \end{array}$

Attempted Reaction of 2 with PbCl₂. A solution of 2 (0.15 g, 0.4 mmol) in 5 mL of THF was poured onto degassed PbCl₂ (0.11 g, 0.4 mmol), and the mixture was stirred at 40 °C, not showing signs of reaction. The red solution was poured away from the yellowish PbCl₂ and evaporated, and the red residue was extracted with hexane, leaving a trace of yellowish powder of presumably PbCl₂. The extract was identified by ¹H and ¹³C NMR to be pure 2.

Reaction of 2 with HCl To Give 3. A solution of 2 (0.13 g, 0.34 mmol) in 10 mL of hexane was cooled with liquid nitrogen, and about 1 mmol of gaseous HCl was added by condensing on a vacuum line. This mixture was slowly warmed to room temperature while being stirred. A fine brown crystalline product separated from an ocher mother liquor. The mother liquor was decanted into another ampule and cooled with liquid nitrogen in order to condense all excess HCl. The crystalline solid was dried under vacuum and then dissolved in toluene to give a brownred solution. This was concentrated to saturation and cooled to -5 °C for 4 days. A polycrystalline solid was separated, washed with cold toluene, and dried under vacuum. Yield: 0.13 g (84%).

Data for 3 are as follows. Mp: 172 °C. EI-MS (160 °C): m/z (relative abundance, %) 456 (M⁺; 4), 424 (17), 423 (55), 422 (49), 421 ([M -Cl]⁺; 100), 420 (23), 419 (27), 405 ([M - Cl - MeH]⁺; 8), 229 (8), 227 (16), 219 (15), 218 (17), 217 ($[M - Cl - C_5Me_4(CH_2)_6]^+$; 34), 216 (11), 215 (14), 214 (7), 213 (24), 181 ([M - Cl - C₅Me₄(CH₂)₆ - $HCl]^+$; 6), 135 (10), 119 (14), 92 (12), 91 (20). ¹H NMR (C₆D₆): 1.28–1.38 (m, 2H, γ -CH₂); 1.38–1.56 (m, 6H, δ -CH₂ and β -CH₂); 1.98, 2.00 (2 \times s, 2 \times 12H, C₅Me₄); 2.20–2.29 (m, 4H, α -CH₂). ¹³C{¹H} NMR (C₆D₆): 13.84, 14.70 (C₅Me₄); 20.19 (δ -CH₂); 24.76 $(\alpha$ -CH₂); 25.87 (β -CH₂); 27.99 (γ -CH₂); 126.00 (C_{ipso}); 130.41, 130.70 (C_{q} , C_5 Me₄). gCOSY (C_6D_6): ¹H/¹H 1.28–1.38/1.38–1.56 $(\gamma - CH_2/\delta - CH_2)$ and $\beta - CH_2$; 1.38-1.56/1.28-1.38, 2.20-2.29 (δ -CH₂ and β -CH₂/ γ -CH₂, α -CH₂); 2.20–2.29/1.28–1.38, 1.38–1.56 $(\alpha$ -CH₂/ γ -CH₂, δ -CH₂ and β -CH₂). gHSQC (C₆D₆): ¹H/¹³C $\sim 1.28 - 1.38/27.99 (\gamma - CH_2/\gamma - CH_2); 1.38 - 1.46/20.19 (\delta - CH_2/\delta - CH_2/\delta)$ CH₂); 1.44–1.56/25.87 (β -CH₂/ β -CH₂); 1.98/13.84 (C₅Me₄); 2.00/ 14.70 (C_5Me_4); 2.20–2.29/24.76 (α -CH₂/ α -CH₂). gHMBC (C_6D_6): 1 H/ 13 C (selected) 2.20–2.29/25.87, 27.99, 126.00, 130.41 (α -CH₂/ β -CH₂, γ -CH₂, C_{ipso} ; C_5 Me₄ (C_q)). IR (KBr, cm⁻¹): 2994 (w, sh), 2986 (m), 2958 (m), 2911 (vs), 2863 (m), 2846 (s), 1493 (m), 1484 (m), 1446 (s), 1430 (m), 1384 (m), 1373 (s), 1308 (w), 1198 (vw), 1080 (vw), 1074 (vw), 1021 (m), 813 (w), 794 (vw), 750 (m), 673 (vw), 622 (vw), 410 (s). Anal. Calcd for C₂₅H₃₈Cl₂Ti (457.36): C, 65.65; H, 8.37. Found: C, 65.62; H, 8.40.

Formation of 4 during Thermolysis of 1 at 100 °C. An NMR tube was filled with a solution of 1 (0.04 g) in 1.2 mL of benzene- d_6 and sealed off with a flame. The tube was heated in boiling water, with interruptions reserved for the measurement of ¹H and ¹³C NMR spectra. The spectra revealed major conversion of 1 to 4 accompanied by evolution of methane ($\delta_{\rm H}/\delta_{\rm C}$ 0.15/4.3 ppm) and subsequent conversion of 4 to 2 with evolution of ethene ($\delta_{\rm H}/\delta_{\rm C}$ 5.25/122.9 ppm).²⁰ After 10 h at 100 °C the maximum yield of intermediate 4 was obtained: 1 (14%), 2 (20%), and 4 (66%). Further heating of the mixture to 100 °C for 35 h led to conversion of all 1 and 4 into 2.

Data for 4 are as follows. ¹H NMR (C_6D_6): -0.68 to -0.52 (m, 1H, TiCH₂CH₂); 0.23-0.38 (m, 1H, TiCH₂CH₂); 1.50, 1.70, 1.72, 1.73,

1.74, 1.76, 1.78, 1.84 (8 \times s, 8 \times 3H, C₅Me₄); 1.88–1.97 (m, 1H, $TiCH_2$; 2.08–2.16 (m, 3H, C₅CH₂CH₂CH= and TiCH₂); 2.20–2.28 (m, 4H, C₅CH₂CH₂CHTi and C₅CH₂CH₂CH=); 2.32-2.40 (m, 1H, C₅CH₂CH₂CHTi); 2.77–2.86 (m, 1H, C₅CH₂CH₂CHTi); 2.88–3.00 (m, 1H, C₅CH₂CH₂CHTi); 4.97 (dd, ${}^{3}J_{HH} = 10.2$ Hz, ${}^{4}J_{HH} = 0.9$ Hz, 1H, E-H, = CH_2); 5.05 (dd, ${}^{3}J_{HH}$ = 17.1 Hz, ${}^{4}J_{HH}$ = 1.5 Hz, 1H, Z-H, = CH_2); 5.82 (ddt, ${}^{3}J_{HH} = 17.1$ Hz, ${}^{3}J_{HH} = 10.2$ Hz, ${}^{3}J_{HH} = 6.5$ Hz, 1H, CH=). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆): 1.90 (TiCH₂CH₂); 10.62, 10.64, 11.52, 11.59, 11.63, 11.79 (2C), 12.02 (C₅Me₄); 22.27 (C₅CH₂CH₂CHTi); 26.58 (C₅CH₂CH₂CH=); 34.77 (C₅CH₂CH₂CH=); 48.97 (C₅CH₂-CH₂CHTi); 73.94 (TiCH₂); 96.32 (C₅CH₂CH₂CHTi); 108.20, 109.76, 113.56, 113.90, 114.55 (C_{qv} C_5Me_4); 114.63 (= CH_2); 114.69, 114.78 (C_q, C_5Me_4) ; 118. 33 (C_{ipso}, C_5Me_4) ; 120.86 (C_q, C_5Me_4) ; 135.59 (C_{ipsor}, C_5Me_4) ; 138.99 (CH=). gCOSY (C₆D₆): ¹H/¹H - 0.68 to -0.52/ 0.23 - 0.38, 1.88 - 1.97, 2.08 - 2.16, 2.32 - 2.40 (TiCH₂CH₂ (H^a)/ $TiCH_2CH_2$ (H^b), $TiCH_2$ (H^a), $TiCH_2$ (H^b), $C_5CH_2CH_2CHTi$); 0.23 - 0.38 / -0.68 to -0.52, 1.88 - 1.97, 2.08 - 2.16, 2.32 - 2.40 $(\text{TiCH}_2\text{CH}_2 (H^b)/\text{TiCH}_2\text{CH}_2 (H^a), \text{TiCH}_2 (H^a), \text{TiCH}_2 (H^b),$ $C_5CH_2CH_2CHTi$; 1.88–1.97/–0.68 to –0.52, 0.23–0.38, 2.08–2.16 (TiCH₂ (H^a)/TiCH₂CH₂ (H^a), TiCH₂CH₂ (H^b), TiCH₂ $(H^{\rm b})$; 2.08–2.16/–0.68 to -0.52, 0.23–0.38, 1.88–1.97 (TiCH₂ $(H^{b})/\text{TiCH}_{2}\text{CH}_{2}$ (H^{a}) , TiCH₂CH₂ (H^{b}) , TiCH₂ (H^{a}) ; 2.09–2.15/ 2.22-2.28, 4.97, 5.05, 5.82 ($C_5CH_2CH_2CH=/C_5CH_2CH_2CH=$, $=CH_2$ (E-H), $=CH_2$ (Z-H), CH=); 2.20-2.27/2.77-2.86, 2.88-3.00 (C₅CH₂CH₂CHTi/C₅CH₂CH₂CHTi (H^a), C₅CH₂CH₂CHTi (H^{b}) ; 2.22–2.28/2.09–2.15 (C₅CH₂CH₂CH=/C₅CH₂CH₂CH=); 2.32-2.40/-0.68 to -0.52, 0.23-0.38, 2.77-2.86, 2.88-3.00(C₅CH₂CH₂CHTi/TiCH₂CH₂ (H^a), TiCH₂CH₂ (H^b), C₅CH₂CH₂-CHTi (H^a), C₅CH₂CH₂CHTi (H^b)); 2.77-2.86/2.20-2.27, 2.32-2.40, 2.88-3.00 (C₅CH₂CH₂CHTi (H^a)/C₅CH₂CH₂CHTi, C₅CH₂-CH₂CHTi, C₅CH₂CH₂CHTi (H^b); 2.88–3.00/2.20–2.27, 2.32–2.40, 2.77–2.86 (C₅CH₂CH₂CHTi (H^b)/C₅CH₂CH₂CHTi, C₅CH₂CH₂-CHTi, C₅CH₂CH₂CHTi (H^a); 4.97/2.09–2.15, 5.82 (=CH₂ (E-H)/ $C_5CH_2CH_2CH=$, CH=); 5.05/2.09-2.15, 5.82 (= CH_2 (Z-H)/ $C_5CH_2CH_2CH=$, CH=); 5.82/2.09-2.15, 4.97, 5.05 (CH=/ $C_5CH_2CH_2CH=$, = CH_2 (E-H), = CH_2 (Z-H)). gHSQC (C_6D_6): $^{1}\text{H}/^{13}\text{C}$ (selected signals) -0.68--0.52, 0.23-0.38/1.90 (TiCH₂-CH₂); 1.88-1.97, 2.08-2.16/73.94 (TiCH₂); 2.09-2.15/34.77 (C₅CH₂CH₂CH=); 2.20-2.27/22.27 (C₅CH₂CH₂CHTi); 2.22-2.28/ 26.58 $(C_5CH_2CH_2CH=)$; 2.32-2.40/96.32 $(C_5CH_2CH_2CHTi)$; 2.77-2.86, 2.88-3.00/48.97 (C₅CH₂CH₂CHTi); 4.97, 5.05/114.63 $(=CH_2); 5.82/138.99 (CH=).$

Thermolysis of [TiMe₂Cp*₂] with Tolane. A degassed solution of [TiMe₂Cp*₂] (0.05 g, 0.14 mmol) in 1.0 mL of toluene- d_8 was added to tolane (0.05 g, 0.30 mmol), and the solution that formed was transferred to an NMR tube. This was sealed with a flame and heated to 110 °C for 19 h. The initially yellow solution turned green. ¹H and ¹³C NMR spectra recognized the complete conversion of [TiMe₂Cp*₂] to the singly tucked-in [TiMe(Cp*){C₅Me₄(CH₂)}]^{4c} and methane; however, no products indicating the involvement of tolane were detected.

Photolysis of 1 with Sunlight. A solution of 1 (0.32 g, 0.75 mmol) in toluene (10 mL) in a sealed ampule was exposed to sunlight for 3 weeks. The initially red solution turned yellow-brown. All volatiles were evaporated under vacuum, and the residue was dissolved in hexane. Slow evaporation of hexane to a cooler arm of the ampule yielded well-developed red crystals of **5** in a brown mother liquor. The mother liquor was decanted. The crystals were washed with condensing hexane vapor and dried under vacuum. Yield: 0.12 g (40%).

Data for **5** were identical with those reported (EI-MS, IR, ¹H and ¹³C NMR, and X-ray diffraction unit cell).^{1a} The residue after evaporation of the mother liquor afforded EI-MS spectra indicating the presence of a variety of products, including hydrogenated **1** in addition to an overwhelming amount of **1**.

Computational Details. DFT calculations have been carried out at the Fermi cluster at the J. Heyrovský Institute of Physical Chemistry,

Academy of Sciences of Czech Republic, vvi, using Gaussian 09, Revision B.01.²¹ The geometry optimization of the molecule was done using the B3LYP functional and the 6-31G(d,p) basis set for all atoms. The Hessian required for the geometry optimization was computed analytically before the first step of the optimization stage. The NMR shielding tensor was calculated using the GIAO method²² carried out on the optimized geometry and using the mPW1PW91 functional along with the 6-311+G(2d,p) basis set.

ASSOCIATED CONTENT

Supporting Information. Figures giving the ¹H NMR (500 MHz) spectrum of **2**, ¹³C NMR spectrum (relaxation delay 58 s) of **2**, gCOSY, gHSQC, and gHMBC spectra of **2**, correlation of observed and calculated $\delta_{\rm C}$ values for **2**, ¹H NMR (300 MHz) spectrum of **3**, 1DTOCSY, gHSQC, and gHMBC spectra of **3**, ¹H NMR spectra of thermolyzed **1** in C₆D₆ in a sealed NMR tube at 100 °C, ¹H, ¹³C{¹H}, gCOSY, gHSQC, and gHMBC spectra of a mixture of products (**1**, 14%; **2**, 20%; **4**, 66%) after heating **1** in C₆D₆ to 100 °C for 10 h, and 1DTOCSY spectra of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) For Ti: (a) Horáček, M; Štěpnička, P.; Gyepes, R.; Císařová, I.; Tišlerová, I.; Zemánek, J.; Kubišta, J.; Mach, K. *Chem.Eur. J.* 2000, 6,2397–2408. (b) Lukešová, L.; Štěpnička, P.; Fejfarová, K.; Gyepes, R.; Císařová, I.; Horáček, M.; Kubišta, J.; Mach, K. *Organometallics* 2002, 21,2639–2653. For Zr and Hf: (c) Warren, T. H.; Erker, G.; Fröhlich, R.; Wibbeling, B. *Organometallics* 2000, 19, 127–134. For Zr: (d) Licht, A. I.; Alt, H. G. J. Organomet. Chem. 2002, 648, 134–148.

(2) For Ti: (a) Sato, K.; Nishihara, Y.; Huo, S.; Xi, Z.; Takahashi, T. J. Organomet. Chem. 2001, 633, 18–26. For Zr: (b) Takahashi, T.; Xi, Z.; Nishihara, Y.; Huo, S.; Kasai, K.; Aoyagi, K.; Denisov, V.; Negishi, E. Tetrahedron 1997, 53, 9123–9134. (c) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. J. Am. Chem. Soc. 1991, 113, 6266–6268. For Hf: (d) Negishi, E.; Holms, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. J. Am. Chem. Soc. 1989, 111, 3336–3346. (e) Nishihara, Y.; Ishida, T.; Huo, S.; Takahashi, T. J. Organomet. Chem. 1997, 547, 209–216.

(3) Okuda, J.; du Plooy, K. E.; Toscano, P. J. J. Organomet. Chem. 1995, 495, 195–202.

(4) (a) Bercaw, J. E.; Brintzinger, H. H. J. Am. Chem. Soc. 1971, 93, 2045–2046. (b) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. J. Am. Chem. Soc. 1972, 94, 1219–1238. (c) McDade, C.; Green, J. C.; Bercaw, J. E. Organometallics 1982, 1, 1629–1634. (d) Pinkas, J.; Císařová, I.; Conde, A.; Fandos, R.; Horáček, M.; Kubišta, J.; Mach, K. J. Organomet. Chem. 2009, 694, 1971–1980.

(5) (a) Rausch, M. D.; Boon, W. H.; Alt, H. G. J. Organomet. Chem.
1977, 141, 299–312. (b) Samuel, E.; Maillard, P.; Giannotti, C. J. Organomet. Chem. 1977, 142, 289–298. (c) Alt, H. G.; Rausch, M. D. J. Am. Chem. Soc. 1974, 96, 5936–5937.

(6) (a) Shur, V. B.; Bernadyuk, S. Z.; Burlakov, V. V.; Andrianov, V. G.; Yanovsky, A. I.; Struchkov, Yu. T.; Volpin, M. E. J. Organomet. Chem. 1983, 243, 157–163.
(b) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Volpin, M. E.; Rosenthal, U.; Görls, H. J. Organomet. Chem. 1994, 476, 197–206.

(7) Mach, K., Unpublished observation.

(8) (a) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358–7361.
(b) Ikariya, T.; Ho, S. C. H.; Grubbs, R. H. *Organometallics* **1985**, *4*, 199–200. (c) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406–2413.

(9) (a) Luinstra, G. A.; Teuben, J. H. J. Chem. Soc., Chem. Commun. 1990, 1470–1471. (b) Luinstra, G. A.; Vogelzang, J.; Teuben, J. H. Organometallics 1992, 11, 2273–2281. (c) Pinkas, J.; Císařová, I.; Gyepes, R.; Horáček, M.; Kubišta, J.; Čejka, J.; Gómez-Ruiz, S.; Hey-Hawkins, E.; Mach, K. Organometallics 2008, 27, 5532–5547.

(10) (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. J. Am. Chem. Soc. 1979, 101, 5074–5075. (b) Howard, T. R.; Lee, J. B.; Grubbs, R. H. J. Am. Chem. Soc. 1980, 102, 6876–6878. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. J. Am. Chem. Soc. 1982, 104, 7491–7496. (d) Anslyn, E. V.; Grubbs, R. H. J. Am. Chem. Soc. 1987, 109, 4880–4890.

(11) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. J. Am. Chem. Soc.
1978, 100, 3611–3613. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.;
Harlow, R. L. J. Mol. Catal. 1980, 8, 37–51. (c) Ott, K. C.; Lee, J. B.;
Grubbs, R. H. J. Am. Chem. Soc. 1982, 104, 2942–2944.

(12) The $[TiCl_2Cp_2]/2LiMe$ system producing $[TiMe_2Cp_2]$ has been found to generate $[Ti(=CH_2)Cp_2]$ at mild temperatures (50–70 °C), being relatively air- and water-stable. As such, it is more convenient than Tebbe reagent for organic synthesis application: (a) Petasis, N. A.; Bzowej, E. I. J. Am. Chem. Soc. **1990**, 112, 6392–6394. (b) Petasis, N. A.; Bzowej, E. I. *Tetrahedron Lett.* **1993**, 34, 1721. (c) Petasis, N. A.; Fu, D.-K. Organometallics **1993**, 12, 3776–3780. (d) Berget, P. E.; Schore, N. E. Organometallics **2006**, 25, 552–553.

(13) Gibson, C. P.; Dabbagh, G.; Bertz, S. H. J. Chem. Soc., Chem. Commun. 1988, 603–605.

(14) Synthesis by benzylation of decamethyltitanocene η^3 -allyl cation: (a) Tjaden, E. B.; Casty, G. L.; Stryker, J. M. J. Am. Chem. Soc. **1993**, 115, 9814–9815. Synthesis by free radical alkylation of η^3 -allyl decamethyltitanocene: (b) Casty, G. L.; Stryker, J. M. J. Am. Chem. Soc. **1995**, 117, 7814–7815.

(15) Obtained from [TiCl₂Cp*₂] and 2Li(CH=CH₂): (a) Beckhaus, R.; Thiele, K.-H.; Ströhl, D. J. Organomet. Chem. 1989, 369, 43–54.
(b) Beckhaus, R.; Sang, J.; Wagner, T.; Ganter, B. Organometallics 1996, 15, 1176–1187.

(16) (a) Hawkins, J. M.; Grubbs, R. H. J. Am. Chem. Soc. 1988, 110, 2821–2823. (b) Buchwald, S. L.; Grubbs, R. H. J. Am. Chem. Soc. 1983, 105, 5490–5491.

(17) Upton, T. H.; Rappé, A. K. J. Am. Chem. Soc. 1985, 107, 1206–1218 and references therein.

(18) For reviews see: (a) Takeda, T. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 475–500. (b) Petasis, N. A. In *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 427–447.

(19) Antropiusová, H.; Dosedlová, A.; Hanuš, V.; Mach, K. Transition Met. Chem. (London) **1981**, 6, 90–93.

(20) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organome tallics* **2010**, *29*, 2176–2179.

(21) Frisch, M. J. et al. *Gaussian 09, Revision B.01*; Gaussian, Inc., Wallingford, CT, 2010.

(22) Ditchfield, R. Mol. Phys. 1974, 27, 789-807.