5532 *Organometallics* **2008,** *27,* 5532–5547

Insertion of Internal Alkynes and Ethene into Permethylated Singly Tucked-in Titanocene

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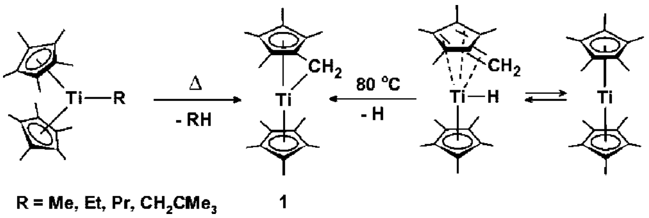
Received July 21, 2008

The singly tucked-in permethyltitanocene **1** reacts with an excess of internal alkynes to give the 1:1 adducts **3a**–**c**,**f**–**i**, arising from insertion of the alkyne triple bond into the titanium–methylene bond. Only the simplest species, 2-butyne, inserted two molecules to give the known compound **2**; however, at a 1:1 stoichiometric ratio the 1:1 adduct **3j** was also smoothly formed. 1,4-Disubstituted conjugated diynes with CMe_3 or $SiMe_3$ substituents reacted in the same way by only one triple bond to give **3d**,**e**, respectively. The dimethylsilylene-bridged dialkynes $Me_2Si(C{\equiv}CR)_2$ (R = $SiMe_3$, CMe_3) afforded compounds **3k**,**l** with both triple bonds reacting. After insertion of the first triple bond, the second one underwent a rearrangement which resulted in substituent shift and formation of a silacyclobutene ring linked to the titanium atom. Alkynes bearing the bulky substituents CMe_3 and $SiMe_3$ were unreactive. Among a number of olefins and 1,3-butadiene, only ethene reacted to give cleanly the 1:1 adduct **3m**. The structures of the paramagnetic $[Ti^{III}(\eta^5\text{-}C_5Me_5)\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CR^1{=}CR^2)\}]$ products **3a**–**g**,**k**,**l** were determined by single-crystal X-ray diffraction analysis. These compounds and compounds **3h**–**j**,**m**, whose crystal structures could not be determined, were chlorinated with $PbCl_2$ to give the diamagnetic products $[Ti^{IV}Cl(\eta^5\text{-}C_5Me_5)\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CR^1{=}CR^2)\}]$ (**4a**–**j**) and the corresponding chlorotitanocene derivatives **4k**–**m**. The solution structures of **4a**–**m** were determined by ^1H and ^{13}C NMR spectroscopy, and crystal structures for **4b**,**e**,**g**,**l**,**m** were found by single crystal X-ray diffraction analysis. DFT calculations threw light on the transition-state molecule for the formation of **3j** and revealed a steric hindrance to be responsible for preventing the insertion of a second molecule of hex-3-yne, the closest homologue of but-2-yne, to react with **3i**, forming a homologue of **2**.

Introduction

Decamethyltitanocene chemistry is well understood, thanks to the pioneering works by Brintzinger and Bercaw[1] and by Teuben.[2] The formation of the paramagnetic singly tucked-in permethyltitanocene $[Ti^{III}\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)]$ (**1**) was first observed when an equilibrium mixture of decamethyltitanocene $[Ti(\eta^5\text{-}C_5Me_5)_2]$ with its singly tucked-in (aka η^6-fulvene) hydride $[TiH\{\eta^6\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)]$ was sublimed under vacuum.[1c] Later on, thermolysis of the decamethyltitanocene monoalkyl compounds $[Ti^{III}R(\eta^5\text{-}C_5Me_5)_2]$ (R = Me, Et, Pr, CH_2CMe_3) appeared to be another clean and convenient method for obtaining **1** (Scheme 1).[2c]

Scheme 1



In both cases the liberation of hydrogen or alkane, respectively, is the only process observed. Only at temperatures above 110 °C does compound **1** lose another atom of hydrogen to give the doubly tucked-in compound $[Ti\{\eta^3{:}\eta^4\text{-}C_5Me_3(CH_2)_2\}(\eta^5\text{-}C_5Me_5)]$, containing one allyl–diene ligand.[2a,c] Compound **1** is a paramagnetic d^1 Ti(III) complex,[1,2] as evidenced by its EPR spectrum ($g = 1.952$, $\Delta H = 70$ G) and the lowest vertical ionization energy of 5.54 eV in He I and He II photoelectron spectra (intensity ratio He II/He I = 1.00) that is typical for a SOMO d(Ti).[3] On the other hand, the electronic absorption spectrum of **1**, showing a single absorption band at λ_{max} 550 nm, is different from the absorption spectra of d^1 titanocene alkyl compounds, which are characterized by two absorptions in about the same region.[2,4] Ultimately, the infrared absorption band of **1** occurring at 3020 cm^{-1} is compatible with the

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(1) (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) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095. (d) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629–1634.

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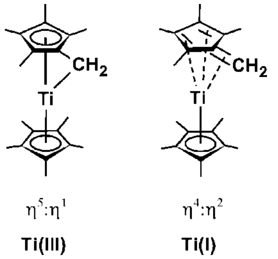
10.1021/om800691f CCC: $40.75

Chart 1



presence of an sp^2 methylene carbon atom that would fit to the fulvene formulation of the ligand.[1,2,5a] Thus, while the unequivocal presence of a Ti(III) atom in **1** is compatible with the η^5:η^1 bonding of the tucked-in ligand, the infrared absorption band for a methylene ν(C$-$H) vibration requires η^4:η^2 bonding (Chart 1).

The crystal structure of **1** was hampered by an extensive disorder[6] and did not aid in distinguishing between both bonding modes. Recently, DFT calculations have shown that compound **1** is a d^1 complex with strongly mixed d and p orbitals, allowing for an sp^2 character of the exo methylene carbon.[7] As we are aware that the electronic structure of **1** cannot be described with either of the two canonical structures of Chart 1, the η^5:η^1 description of **1** will be used throughout the paper to stress that the high reactivity follows from the Ti(III) valence state.

Reactions of **1** with protonic acids, hydrogen, halogens, disulfides, methyl halides, nitriles, and 2-methylpyridine were studied by Pattiasina in his Ph.D thesis and only partly reported in journals.[5] Protonic acids HX such as hydrogen halides, carboxylic acids, alcohols, and pyrrole split the Ti$-$methylene bond to give the Ti(III) decamethyltitanocene derivatives [$\mathrm{Ti^{III}X(\eta^5\text{-}C_5Me_5)_2}$], while hydrogen under mild conditions afforded the simple hydride [$\mathrm{Ti^{III}H(\eta^5\text{-}C_5Me_5)_2}$]. Oxidation with halogens, organic disulfides, or methyl halides gave rise to Ti(IV) products with the preserved Ti$-$methylene bond [$\mathrm{TiX\{\eta^5:\eta^1\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)}$] (X = Br, I, SPh). Methyl halides also acted as oxidation agents, yielding a 1:1 mixture of [$\mathrm{TiX\{\eta^5:\eta^1\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)}$] (X = Cl, Br) and [$\mathrm{TiMe\{\eta^5:\eta^1\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)}$]. *tert*-Butyl cyanide underwent an insertion of the C≡N bond into the Ti$-$methylene bond followed by a proton transfer from the methylene group to the nitrogen atom, giving an unsaturated titanium amide: e.g., [$\mathrm{Ti^{III}\{\eta^5:\eta^1\text{-}C_5Me_4CH{=}C(^tBu)NH\}(\eta^5\text{-}C_5Me_5)}$].[5a,b] The most interesting reaction of **1** was observed for 2-methylpyridine, whose C$-$H bond in an ortho position reacted in an opposite way with respect to protonic acids. The hydrogen atom was transferred to Ti, the carbon atom was linked to the methylene carbon, and the nitrogen atom was coordinated to the metal, thus affording the Ti(III) titanocene hydride stabilized by intramolecular nitrogen coordination.[5c] Recently, compound **1** was shown to react with water to form the titanocene hydroxide [$\mathrm{Ti^{III}OH(\eta^5\text{-}C_5Me_5)_2}$][8a] and with the strong Lewis acid $\mathrm{B(C_6F_5)_3}$ to give the paramagnetic zwitterionic complex [$\mathrm{(Ti^{III})^+(\eta^5\text{-}C_5Me_5)\{\eta^5\text{-}C_5Me_4CH_2B^-(C_6F_5)_3\}}$] (Scheme 2).[8b]

In spite of the aforementioned interest in the reactivity of **1**, this compound has not been examined for its reactivity toward internal alkynes and olefins. We have entered an investigation of this topic in an effort to find out the mechanism of formation of the interesting paramagnetic product **2**, which formed in high yield when [$\mathrm{TiCl_2(\eta^5\text{-}C_5Me_5)_2}$] was reduced with an excess of magnesium in the presence of excess but-2-yne in tetrahydrofuran (Scheme 3).[9]

The formation of **2** could be envisaged as resulting from insertion of two molecules of but-2-yne into the titanium$-$methylene bond of **1** transiently generated in the reaction mixture. Following this suggestion, we have undertaken the investigation of ability of **1** to undergo insertion reactions with but-2-yne and a number of other internal alkynes, conjugated and bridged dialkynes, and simple olefins. The structures of the Ti(III) insertion products as depending on the nature of the alkyne substituents, chlorination of the Ti(III) products with $\mathrm{PbCl_2}$[10] in order to obtain the Ti(IV) derivatives accessible to high-resolution NMR methods, and consideration of the insertion mechanism on the basis of DFT calculations are reported herein.

Results and Discussion

Compound **1** was obtained from [$\mathrm{TiCl_2(\eta^5\text{-}C_5Me_5)_2}$] by a known procedure[2] via titanocene chloride and titanocene monomethyl and thermolysis in toluene at 110 °C (Scheme 4).

The purple crystalline product was purified by recrystallization from hexane and gave spectroscopic data[1−5] and molecular parameters that are published elsewhere.[6] The solution of **1** in hexane was reacted with simple internal alkynes, head-to-tail dimers of pent-1-yne, *tert*-butylethyne, and (trimethylsilyl)ethyne, 1,4-disubstituted 1,3-diynes, and dimethylsilylene-bridged alkynes, as well as with ethene, but-1-ene, but-2-ene, *tert*-butylethene, cyclopentene, and buta-1,3-diene. In all cases the alkynes or alkenes were used in a 2$-$10-fold molar excess with respect to **1**. Among the internal alkynes but-2-yne reacted quickly at room temperature, causing the color of **1** to change from purple to brownish yellow and finally to the green color of the known compound **2**, containing two but-2-yne molecules inserted (Scheme 2).[9] In contrast, all the other reacting internal alkynes, including the nearest homologue, hex-3-yne, afforded the brownish yellow products **3a$-$i** with only one alkyne molecule inserted. The 1:1 insertion product of but-2-yne, **3j**, was obtained when only 1 molar equiv of the alkyne was dissolved from the gas phase in a stirred hexane solution of **1** (Scheme 5).

The reactions were accomplished within hours at room temperature, except for the case of a head-to-tail dimer of (trimethylsilyl)ethyne, $\mathrm{Me_3SiC{\equiv}CC(SiMe_3){=}CH_2}$, which required warming to 60 °C for 3 h to yield **3g**. The alkynes with very bulky substituents such as bis(trimethylsilyl)ethyne, (trimethylsilyl)*tert*-butylethyne, and the head-to-tail dimer of *tert*-butylethyne, *t*-BuC≡CC-*t*-Bu═CH$_2$, did not react even after heating to 80 °C for 3 days.

The dimethylsilylene-bridged dialkynes $\mathrm{Me_2Si(C{\equiv}CSiMe_3)_2}$ and $\mathrm{Me_2Si(C{\equiv}C\text{-}}t\mathrm{\text{-}Bu)_2}$ reacted smoothly with **1** using both triple bonds for the insertion combined with a rearrangement to give the 1-silacyclobut-2-ene moiety (Scheme 6).

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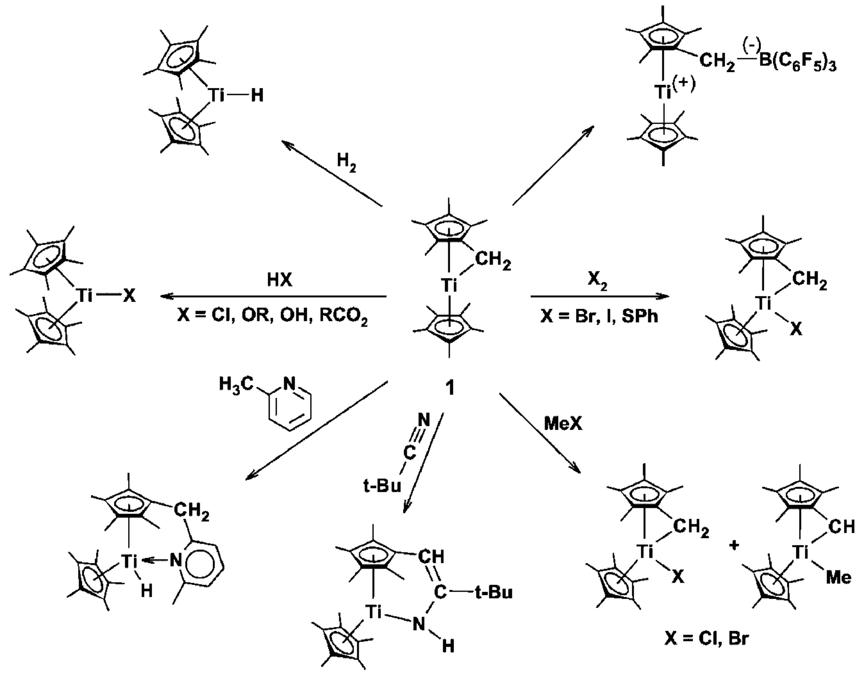
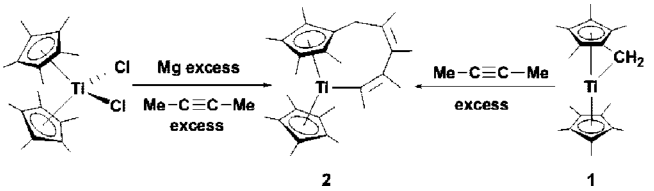
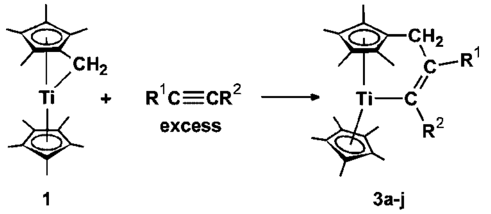
Scheme 2. Reactivity of 1



Scheme 3



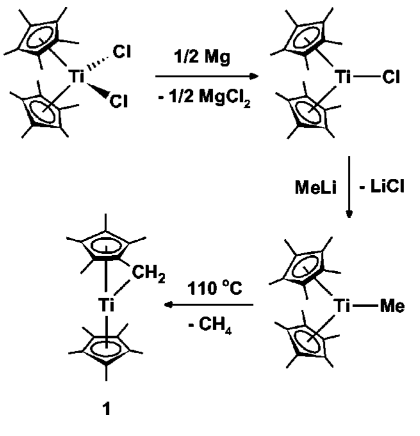
Scheme 5. Preparation of 3a−j



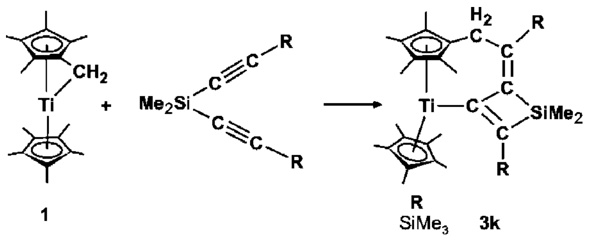
	R^1	R^2
3a	Ph	Ph
3b	Me	$SiMe_3$
3c	Ph	$SiMe_3$
3c'	$SiMe_3$	Ph
3d	CMe_3	$C{\equiv}CCMe_3$
3e	$SiMe_3$	$C{\equiv}CSiMe_3$
3f	Pr	$C(Pr){=}CH_2$
3g	C(SiMe3)=CH_2	$SiMe_3$
3h	Me	Ph
3i	Et	Et
3j*	Me	Me

* **1**: MeC≡CMe = 1:1

Scheme 4. Synthetic Route to 1



Scheme 6



R	
$SiMe_3$	**3k**
t-Bu	**3l**

Rearrangement involving the shift of the $SiMe_3$ group for **3k** or *t*-Bu group for **3l** and ring closure apparently had to follow the insertion of the first triple bond (Scheme 7).

The formation of fused zirconacyclobutene−silacyclobutene[11] and titanacyclobutene−silacyclobutene[12] complexes (Chart 2, **A**) was observed in the reactions of the metallocene at the onset of their formation with various $R_2Si(C{\equiv}CR')_2$ derivatives. Also, spiro dimetallacyclobutene−silacyclobutene complexes sharing the silicon atom (Chart 2, **B**) were prepared analogously using tetraalkynylsilanes.[13] It is of interest that the permethyltitanocene−

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[11] (a) Takahashi, H.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665–2666. (b) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, H. *J. Am. Chem. Soc.* **1997**, *119*, 12842–12848.

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Scheme 7. Suggested Mechanism of the Formation of 3k,l

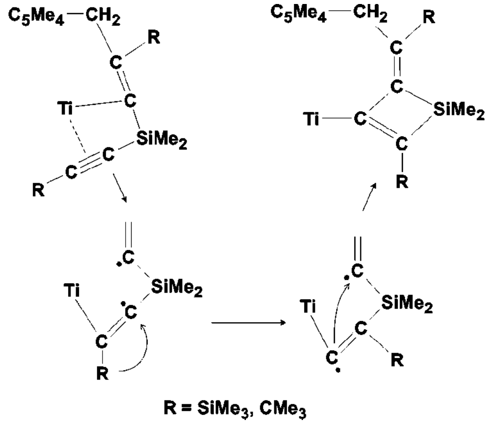
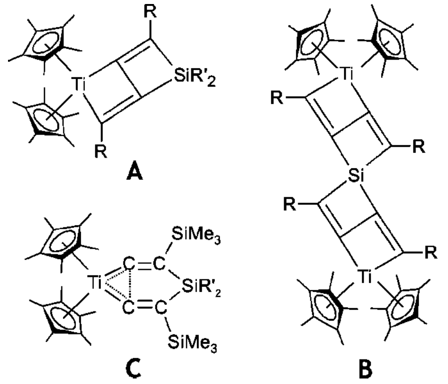
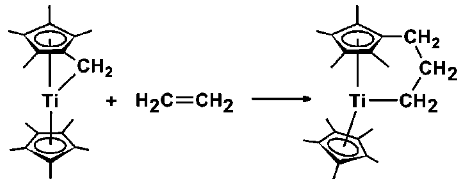


Chart 2



Scheme 8



1 **3m**

bis(trimethylsilyl)ethyne complex reacted with $Me_2Si(C{\equiv}CSiMe_3)_2$ to give a different 1-titana-4,4-dimethyl-4-sila-3,5-bis(trimethylsilyl)cyclohexa-2,5-diene complex (Chart 2, **C**)[14] and was unreactive to $Me_2Si(C{\equiv}C\text{-}t\text{-}Bu)_2$.[12] On the other hand, compounds **3d**,**e**, possessing one free triple bond, did not react with added **1**, even at 80 °C, apparently due to some steric congestion.

Of the olefins only ethene reacted with **1** to give the ocher product **3m**, containing one ethene molecule inserted (Scheme 8). The other olefins and 1,3-butadiene appeared to be nonreactive, even after heating to 80 °C for 3 days.

The limited reactivity of **1** toward sterically hindered internal alkynes and olefins becomes understandable after comparing it with the reactivity of $[Ti^{III}Me(\eta^5\text{-}C_5Me_5)_2]$ (**5**), the precursor of **1**. The methyl permethyltitanocene **5** did not react with ethene, even at high pressure and 100 °C, and among internal alkynes it reacted only with but-2-yne, which inserted one molecule into the Ti−Me bond to give $[Ti^{III}C(Me){=}CMe_2(\eta^5\text{-}C_5Me_5)_2]$.[10b] This comparison shows that the presence of a methyl group in the pseudoequatorial plane of **5** apparently hinders coordination of alkynes more bulky than but-2-yne, and as far as ethene insertion is concerned, the alkyltitanocene products formed can be higher in energy than **5**.[15] Although the insertion reactions into the Ti−C bond are very similar in both cases, compound **1** affords more coordination space than **5**, the methylene group with sp^2-hybridized carbon atom is more easily activated to form a transition complex than the methyl group in **5**, and the intramolecular tether formed is capable of stabilizing the product more than a titanium-linked pending alkenyl or alkyl chain.

All the products **3a**−**m** displayed EPR spectra in solution ($g = 1.942{-}1.962$, $\Delta H = 10{-}40$ G) and frozen toluene glass, and electronic absorption spectra showed two absorptions in the visible region (440−500 and 560−680 nm) (see the Supporting Information). Both types of spectra resembled the spectra of Ti^{III} permethyltitanocene alkyl[2,4,16] or halide compounds[4,17] with trigonal coordination of the titanium atom. The crystal structure investigation of **3a**−**g** (see below) found that such a coordination is only slightly asymmetrical in compounds **3**. All compounds purified by crystallization were characterized by EI-MS spectra, which mainly showed abundant molecular ions ($M^{\bullet+}$) and ions of **1** after elimination of the alkynes (L) ($[M - L]^+$). The low abundance of $M^{\bullet+}$ for **3g** (22%) is probably due to a partial thermal dissociation of the alkyne, whose ions $L^{\bullet+}$ and $[L - Me]^+$ are also abundant. Uncertainty about the molecular ion of **3m** in standard EI-MS spectra at IP 70 eV showing $[M - 4\ H]^+$ to be the base peak were solved by measuring with IP of 15 eV which gave $M^{\bullet+}$ the base peak; however, the abundant loss of hydrogen atoms from $M^{\bullet+}$ remained remarkable. The IR spectra gave clear evidence for the presence of groups such as Ph (**3a**,**c**), $SiMe_3$ (**3b**,**c**,**e**,**g**), *t*-Bu (**3d**), C≡C (**3d**,**e**), and $C{=}CH_2$ (**3f**,**g**); however, the $\nu(C{=}C)$ vibration that should be present for all the compounds except **3m** was of very low intensity in the range 1590−1510 cm^{-1} and in some cases was even not discernible or was hidden under the absorption bands of the Ph group. Due to paramagnetic broadening and resonance line shifts the ^1H and ^{13}C NMR spectra were not applicable for resolution of different substituents in the inserted alkyne. Therefore, the majority of the products were analyzed by single-crystal X-ray diffraction, which allowed us to unequivocally identify the position of substituents in compounds **3a**−**g**, as shown in Scheme 4, and the structures of **3k**,**l**, as shown in Scheme 5 (see below).

Diamagnetic Chlorinated Compounds 4a−m. Since the products **3h**−**j**,**m** did not give crystals suitable for X-ray single-crystal analysis, these and all other compounds **3** (**3a**−**g**,**k**,**l**) were converted to the chlorotitanium(IV) compounds **4a**−**m** by chlorination with $PbCl_2$ (Scheme 9)[10] in order to attempt the structure resolution by means of ^1H and ^{13}C NMR spectroscopy.

All the compounds were red diamagnetic solids which were somewhat less sensitive to air and humidity than their precursors **3a**−**m**. Their color arose from two absorption bands occurring in the ranges 395−490 and 475−660 nm (see the Supporting Information). Their electronic absorption spectra were similar

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[15] In our hands reaction of **5** with ethene at 60 °C for 3 days gave a trace of polyethene and higher olefins and the $[Ti^{II}(C_2H_4)\{\eta^5\text{-}C_5Me_5)_2]$ complex[20a] was the only one isolated from a mixture of products.

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Scheme 9. Chlorination of 3a−m and Structure of the Products 4a−m

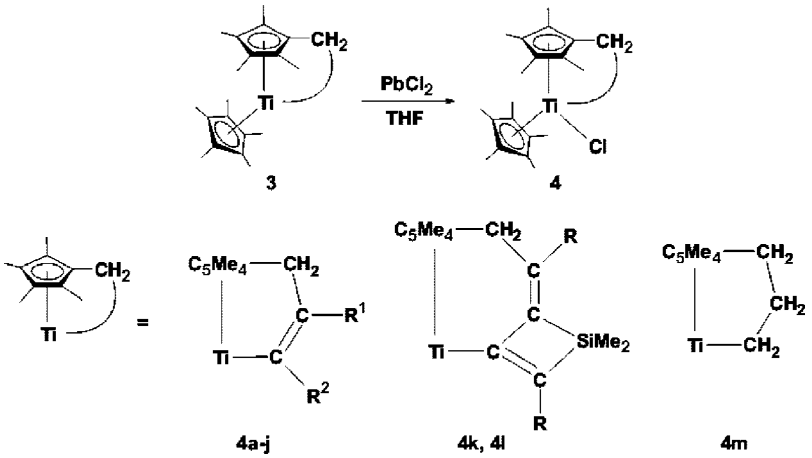

Table 1. Selected ^{1}H and ^{13}C NMR Resonances (in ppm) of Compounds 4a−j[a]

compd	C(21)R^1	C(22)R^2	^{1}H C(6)H_2 ($^2J_{HH}$, Hz)	C(6)	C(21)	C(22)
4a	Ph	Ph	3.14, 3.44 (17.1)	37.77	157.35	204.41
4b	Me	$SiMe_3$	2.81, 2.93 (17.4)	40.47	157.39	212.91
4c′	$SiMe_3$	Ph	2.91, 3.25 (16.8)	36.32	163.63	221.96
4c	Ph	$SiMe_3$	2.89, 3.16 (18.6)	43.27	161.03	215.05
4d	CMe_3	$C{\equiv}CCMe_3$	2.86, 3.12 (18.6)	37.97	164.05	178.45
4e	$SiMe_3$	$C{\equiv}CSiMe_3$	2.78, 3.00 (18.6)	35.31	166.79	195.11
4f	*n*-Pr	$C({=}CH_2)(CH_2)_2CH_3$	2.94, 3.02 (17.4)	34.96	160.93	208.90
4g	$C(SiMe_3){=}CH_2$	$SiMe_3$	3.07, 3.22 (17.4)	40.93	166.03	215.54
4h	Me	Ph	2.92, 3.00 (17.4)	37.88	157.32	207.17
4i	Et	Et	2.76, 2.84 (16.8)	32.45	149.25	212.45
4j	Me	Me	2.75	36.43	143.48	206.98

[a] Crystallographic atom labeling.

to those of highly methyl-substituted titanocene dichlorides.[18] The EI-MS spectra of compounds **4** showed the molecular ions in low to moderate abundance, except for **4g**, whose molecular ion easily eliminated the alkyne ligand (L) and was not observed. The $[C_5Me_5TiCl]^+$ ion was a base peak for all compounds except **4a**, where the $[M - C_5Me_4CH_2]^+$ ion surprisingly dominated. Less pronounced fragment ions indicated elimination of HCl, L, or specific groups of alkynes. Infrared spectra afforded very similar information about the presence of specific groups, such as the spectra of nonchlorinated precursors. Decisive information on the structure of compounds **4** was obtained from their NMR spectra, and this was corroborated by crystal structures of **4b**,**e**,**g**,**m**.

^{1}H and ^{13}C NMR spectra of compounds **4** displayed some general features which are summarized in Table 1. Due to the stereogenic center at the titanium atom, the protons on C(6)H_2 are diastereotopic, giving rise to two doublets in the region 2.7−3.4 ppm with geminal coupling constants $^2J_{HH} = 16.8-18.6$ Hz. A high value of $^2J_{HH}$ together with ^{13}C chemical shifs of C(6) are consistent with sp^3 hybridization of the C(6) carbon. The methyl groups in the tethered C_5Me_4 ring gave rise to four signals in both ^{1}H and ^{13}C NMR spectra. Among them, a relatively large downfield shift of one methyl group signal is noteworthy. On the basis of gHMBC and 1D NOESY spectra, this signal is assigned to the methyl group in a position vicinal to C_{ipso}, close to the Ti−Cl bond (C7 in Figure 5), which induced its anisotropic deshielding. Although anisotropic deshielding due to the C(21)−C(22) double bond could also be considered, such an effect had to be marginal, because a similar methyl downfield shift was observed in **4m**, where the double bond is absent. Signals for the permethylcyclopentadienyl ring fall into a narrow region in ^{1}H as well as in ^{13}C spectra (C_5Me_5, δ_H 1.62−1.96 ppm, δ_C 12.66−13.02 ppm; C_5Me_5, δ_C 122.96−125.47 ppm), remaining almost unaffected by the rest of the molecule. The chemical shifts of TiC(22)=C(21) quaternary carbons (Table 1) in ^{13}C NMR spectra are close to those reported previously for permethyltitanocene−alkenyl species, the titanium-linked C(22) being shifted far more downfield.[10b,19]

The positions of substituents R^1 and R^2 were assigned on the basis of 1D NOESY experiments, where irradiation of C(6)H_2 protons enhanced the signal(s) of the substituent at the C(21) atom, provided it was bearing proton(s) (see the Supporting Information). Thus, determined substituent positions were consistent with those determined by X-ray diffraction analysis for compounds **4b**,**e**,**g** and **3a**−**g**, except for **3c**. Unlike all other cases, only the crystalline **3c** was obtained in low yield (23%), and thus not the pure **3c** but the mother liquor was used for the chlorination. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the chlorination product revealed the presence of two regioisomers (Table 1), and the 1D NOESY experiment assigned the more abundant isomer to **4c′** (85%). The irradiation of the high-field proton (2.91 ppm) of C(6)H_2 gave rise to the signal for the SiMe_3 group (−0.06 ppm) and the signal of the methyl group in a

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(18) (a) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406–2413. (b) Horáček, M.; Gyepes, R.; Císařová, I.; Polášek, M.; Varga, V.; Mach, K. *Collect. Czech. Chem. Commun.* **1996**, *61*, 1307–1320.

(19) (a) Cohen, S. A.; Bercaw, J. E *Organometallics* **1985**, *4*, 1006–1014. (b) Beckhaus, R.; Sang, J.; Oster, J.; Wagner, T. *J. Organomet. Chem.* **1994**, *484*, 179–190. (c) Beckhaus, R.; Strauss, I.; Wagner, T. *J. Organomet. Chem.* **1994**, *464*, 155–161. (d) Beckhaus, R.; Sang, J.; Wagner, T.; Ganter, B. *Organometallics* **1996**, *15*, 1176–1187. (e) Beckhaus, R.; Wagner, T.; Burlakov, V. V.; Baumann, W.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 129–134. (f) Thomas, D.; Peulecke, N.; Burlakov, V. V.; Heller, D.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U.; Beckhaus, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 919–924.

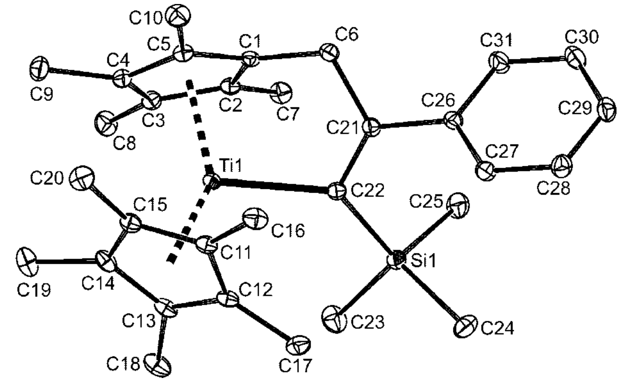

Figure 1. PLATON[30] drawing of **3c** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

position vicinal to $\mathrm{C_{ipso}}$, remote from the Ti−Cl bond (C10 in Figure 5) (1.85 ppm), in addition to the second signal (3.25 ppm) of $\mathrm{C(6)}H_2$. Subsequent irradiation of the downfield proton (3.25 ppm) of $\mathrm{C(6)}H_2$ gave rise to the signals of the $\mathrm{Si}Me_3$ group (−0.06 ppm), the permethylcyclopentadienyl ligand (1.62 ppm), and the methyl group in a position vicinal to $\mathrm{C_{ipso}}$, close to the Ti−Cl bond (C7 in Figure 5) (2.62 ppm), in addition to the signal of $\mathrm{C(6)}H_2$ at 2.91 ppm. The NMR assessment of **4c** (15%) and **4c′** (85%) allowed us to determine the abundance of the formed regioisomers **3c** and **3c′**. Assuming that **3c** (23%) was removed by crystallization before the chlorination, the crude insertion product should consist of **3c** (35%) and **3c′** (65%).

The ^{1}H and ^{13}C NMR spectra revealed the presence of alkynyl groups on C(22) in **4d**,**e** displaying resonances typical for quaternary acetylenic carbons (89.58 and 113.02 ppm for **4d**; 106.69 and 115.60 ppm for **4e**). The presence of a $=\mathrm{CH_2}$ group in **4f**,**g** was also unequivocally detected (**4f**, δ_H 4.35, 4.77 ppm, δ_C 106.31 ppm; **4g**, δ_H 5.39, 5.75, δ_C 127.08), showing the signal of the upfield shifted methylene proton to be significantly broadened in the both complexes. For **4g**, the signal of $C_5\mathrm{Me}_5$ at δ_C 124.14 ppm, C(22) at δ_C 215.54 ppm, and the signal at −14.13 ppm in the ^{29}Si NMR spectrum were also broadened.

Complexes **4k**,**l** contained a silacyclobutene ring taking part in their tether chains. Their quaternary carbon atoms directly linked to titanium were shifted highly downfield, δ_C 264.56 ppm for **4k** and δ_C 240.69 ppm for **4l**, whereas the other sp^2 quaternary carbon atoms resonated as expected.[19]

The trimethylene chain in **4m** displayed three resonances at δ_C 25.64, 44.67, and 80.58 ppm. The last one falls into the range of δ_C for an sp^3 carbon linked to the titanium atom.[20] The proton signals of the methylene groups are rather complicated, due to the presence of a stereogenic titanium center. The highly upfield shifted signal at −0.42 ppm was attributed to the hydrogen atom of the $\mathrm{TiCH_2}$ group, which is directed toward the Ti−Cl bond.

Crystal Structures of 3a−g. The crystal structures of **3a**−**g** are generally uniform, resembling the trigonal coordination of the central atom known for Ti^{III} permethyltitanocene monosubstituted complexes. The selected PLATON drawings of compounds **3c** (Figure 1), **3e** (Figure 2), **3f** (Figure 3), and **3g** (Figure 4) represent various types of alkyne products; however, the geometry of the inserted disubstituted alkenylene moiety is only moderately affected by the substituents R^1 and R^2 at the C(21) and C(22) carbon atoms. The substituents were found in the

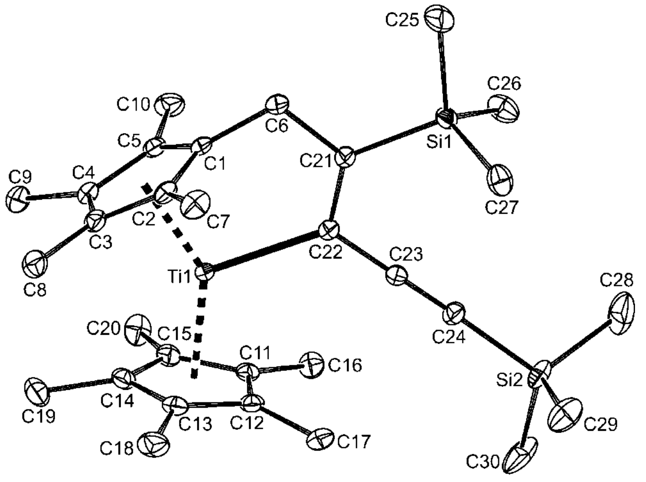

Figure 2. PLATON[30] drawing of **3e** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

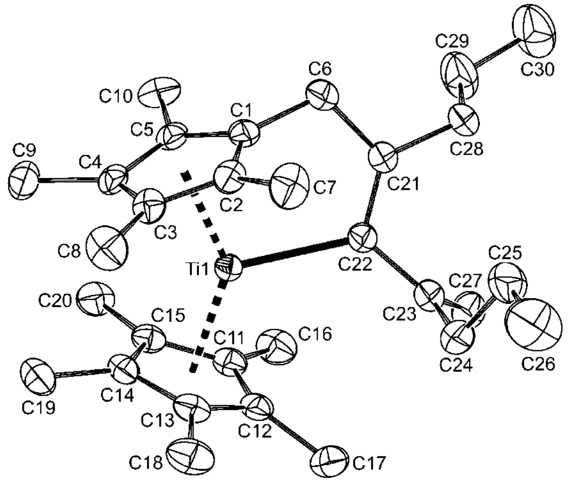

Figure 3. PLATON[30] drawing of **3f** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

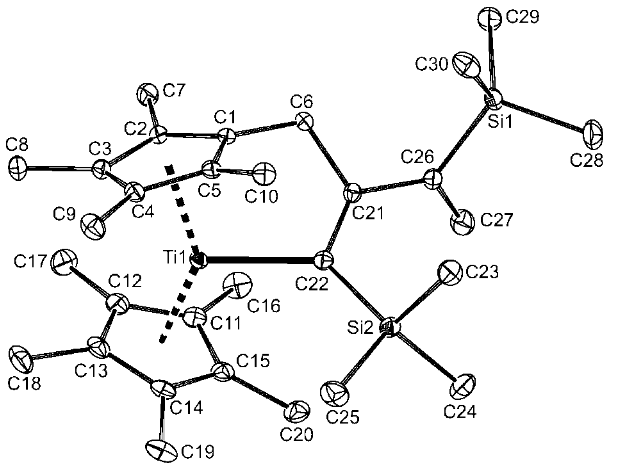

Figure 4. PLATON[30] drawing of **3g** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

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(20) (a) Cohen, S. A.; Auburn, P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136–1143. (b) Lukešová, L.; Horáček, M.; Štěpnička, P.; Gyepes, R.; Císařová, I.; Kubišta, J.; Mach, K. *J. Organomet. Chem.* **2004**, *689*, 1919–1929. (c) Horáček, M.; Štěpnička, P.; Kubišta, J.; Císařová, I.; Petrusová, L.; Mach, K. *J. Organomet. Chem.* **2003**, *667*, 154–166. (d) Horáček, M.; Štěpnička, P.; Gyepes, R.; Císařová, I.; Tišlerová, I.; Zemánek, J.; Kubišta, J.; Mach, K. *Chem. Eur. J.* **2000**, *6*, 2397–2408.

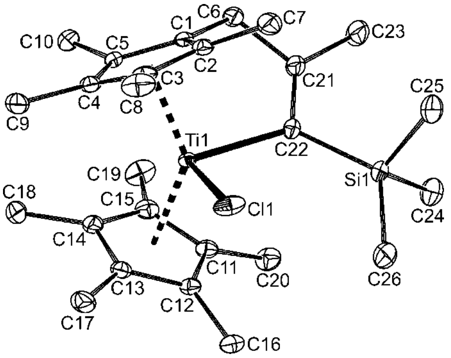

Figure 5. PLATON[30] drawing of **4b** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

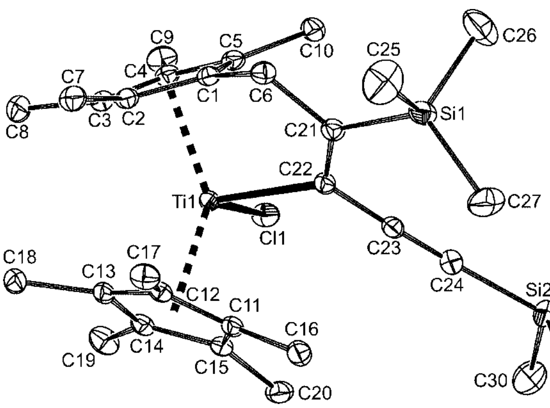

Figure 6. PLATON[30] drawing of **4e** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

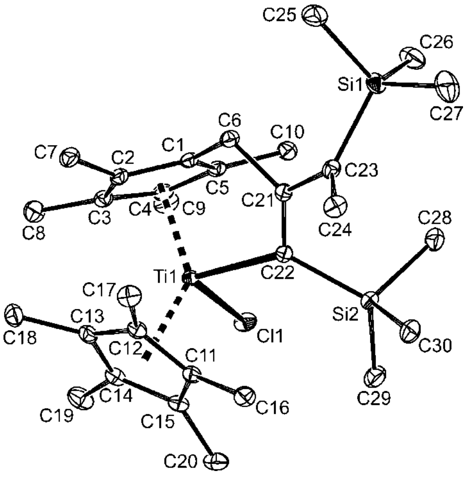

Figure 7. PLATON[30] drawing of **4g** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

positions indicated in Scheme 5. The geometric parameters gathered in Table 2 show that the tethered cyclopentadienyl ligand is more tightly bound to the titanium atom than the intact ligand (Ti−Cg(1) = 2.033(2)−2.0561(15) Å versus Ti−Cg(2) = 2.062(3)−2.0885(15) Å), confirming the presence of the double bond (C(21)=C(22) = 1.354(6)−1.369(7) Å) and its linking to the titanium atom (Ti−C(22) = 2.201(5)−2.280(2) Å) and the methylene carbon (C(6)−C(21) = 1.497(3)−1.5338(19) Å). The angles in the tethered alkenylene system are versatile, allowing for a moderate variation in the Cg(1)−Ti−Cg(2), Cg(1)−Ti−C(22), Ti−C(22)−C(21), and C(22)−C(21)−C(6) angles.

The tether bond Ti−C(22) is inclined to the Cg(1) cyclopentadienyl ring, as the Cg(1)−Ti−C(22) angle is ca. 12−15° smaller than Cg(2)−Ti−C(22). The substituted Ti−C-(R^1)=C(R^2)−- moiety in **3a**−**g** is only slightly more bent than the Ti−CH=CH$_2$ group in Cp*$_2$Ti(L)CH=CH$_2$ (L = F, OR) compounds.[19b,c] The geometry of the tether is influenced by their substituents, however. At least, the Ti−C(22)−C(21) angle is markedly larger than the C(22)−C(21)−C(6) angle when the carbon atom C(22) is carrying a trimethylsilyl group (**3b**,**c**,**g**).The torsion angles at the double bond (τ = Ti−C(22)−C(21)−C(6) and ω involving the substituent atoms (C or Si) at C(22)−C(21)) indicate a nearly planar arrangement for **3a**,**e**; however, in other compounds these angles approach up to 30° (see Table 2). This deviation from double-bond planarity together with a somewhat elongated C=C bond is due to the vicinity of the transition metal.

Crystal Structures of 4b,e,g,m. PLATON drawings of **4b**,**e**,**g**,**m** are shown in Figures 5−8, respectively, and their common geometric parameters are given in Table 3. The parameters for **4b**,**e**,**g** can be compared with the corresponding parameters for their Ti(III) precursors (cf. Table 2). The chlorine atom occupies roughly the equatorial position, as indicated by the mutually close magnitudes of the Cg(1)−Ti−Cl and Cg(2)−Ti−Cl angles. The Ti−Cl bond lengths 2.3267(5)−2.3442(6) Å are slightly shorter than the bonds in [TiCl$_2$(η^5-C$_5$Me$_5$)$_2$] (average 2.349(1) Å),[21a] [TiCl$_2$(η^5-C$_5$Me$_4$-*t*-Bu)$_2$] (2.3666(4) Å),[21b] and [TiCl$_2$(η^5-C$_5$Me$_4$SiMe$_3$)$_2$] (2.365(1) Å).[18b] The chlorine addition brought about a slight increase in all bond lengths, which were influenced by a larger coordination number of the metal.

The pseudotetrahedral coordination of the titanium atom accounts for the smaller Cg(1)−Ti−Cg(2) angles and a smaller difference in the Cg(1)−Ti−C(22) and Cg(2)−Ti−C(22) angles. The tether geometry is changed only slightly from the tether geometry for their precursors. Compound **4m** differs from the above structures by the tether being composed of only sp^3 carbon atoms. Due to this, the Ti−C(22) is discernibly shorter, the bond lengths C(21)−C(22) and C(21)−C(6) are virtually equal, and the valence angles at C(21) and C(22) are close to tetrahedral.

Crystal Structures of 3k,l and 4l. The unit cells of **3k** and **3l** contained two independent molecules whose geometric parameters differed only slightly; therefore the geometry of molecules 1 will be discussed only. The PLATON drawing for molecule 1 of **3l** is shown in Figure 9 and that for **4l** in Figure 10.

The selected geometric parameters for **3k** (molecule 1), **3l** (molecule 1) (molecules 1 are labeled using prefix 1), and **4l** are given in Table 4. As for **3a**−**g** the Ti−Cg(11) distances in **3k**,**l** are shorter than the Ti−Cg(12) distances and the Cg(11)−Ti−C(123) angles are smaller than those involving Cg(12). The tether between the cyclopentadienyl ring and the titanium atom is longer by one carbon. An additional C−C bond (C(123)−C(122)) forms a saturated side of the formed silacyclobutene moiety. Its geometry is similar to those involved in the fused titanacyclobutene−silacyclobutene moieties:[12,13] the angle at the Si atom is about 75°, whereas that at the opposite carbon atom C(123) is above 100°. The double bond C(123)−C(124) forming the silacyclobutene cycle (1.386(2) Å for **3k** and 1.376(3) Å for **3l**) is markedly longer than the analogous double bond in titanacyclobutene compounds.[19b,c] On the other hand, the exocyclic double bond C(121)−C(122) is shorter than the

Table 2. Important Common Bond Lengths (Å) and Valence and Dihedral Angles (deg) for 3a−g

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
Bond Lengths (Å)							
Ti−Cg(1)^a	2.0499(10)	2.033(2)	2.0471(7)	2.037(2)	2.0436(9)	2.0561(15)	2.0359(7)
Ti−Cg(2)^a	2.0777(10)	2.0782(18)	2.0731(7)	2.062(3)	2.0672(9)	2.0885(15)	2.0801(7)
Ti−C(22)	2.280(2)	2.246(3)	2.2512(15)	2.201(5)	2.2604(18)	2.265(3)	2.2423(14)
C(21)−C(22)	1.355(3)	1.355(5)	1.364(2)	1.369(7)	1.354(6)	1.361(4)	1.3627(19)
C(6)-C21)	1.497(3)	1.530(5)	1.529(2)	1.518(7)	1.508(6)	1.500(5)	1.5338(19)
Valence Angles (deg)							
Cg(1)−Ti−Cg(2)	139.90(4)	141.81(8)	141.83(3)	145.86(11)	142.03(3)	140.32(6)	141.73(3)
Cg(1)−Ti−C(22)	103.17(6)	101.40(12)	102.40(4)	100.39(14)	103.61(5)	103.62(9)	102.07(4)
Cg(2)−Ti−C(22)	116.91(6)	116.61(12)	114.68(4)	113.34(14)	114.36(5)	115.89(9)	115.37(4)
Ti−C(22)−C(21	117.83(15)	109.5(2)	108.34(10)	117.0(3)	120.84(12)	116.6(2)	108.43(10)
C(22)−C(21)−C(6)	120.35(19)	121.8(3)	122.12(13)	116.7(4)	117.61(16)	119.7(3)	122.20(12)
Dihedral Angles (deg)							
φ^b	35.91(12)	33.70(19)	33.22(5)	31.97(16)	34.89(7)	36.24(9)	33.57(4)
τ^c	0.1(3)	28.2(4)	−24.57(17)	20.0(6)	−3.4(2)	14.4(4)	25.23(16)
ω^d	4.5(3)	28.3(4)	−29.5(2)	13.2(6)	−2.1(2)	11.0(5)	30.03(19)

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(11−15) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares planes of cyclopentadienyl rings. [c] Dihedral angle Ti−C(22)−C(21)−C(6). [d] Dihedral angle involving C(21) and C(22) and attached atoms (C or Si) of their substituents.

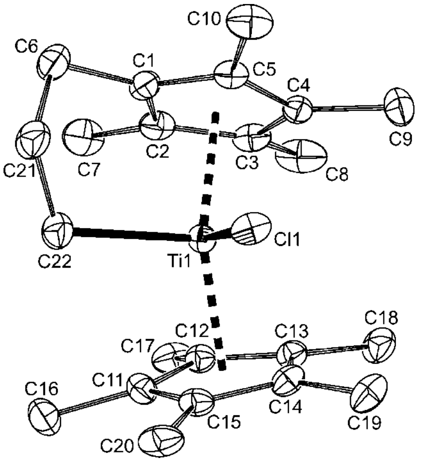

Figure 8. PLATON[30] drawing of **4m** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

double bonds in **3a−g**, due to its remoteness from the metal. In **4l**, addition of the chlorine atom at a roughly equatorial position resulted in a slight prolongation of all bonds which were influenced by an increased coordination number of the metal. The geometry of the silacyclobutene ring and the overall geometry of the tether moiety were changed rather negligibly, however.

Insertion Mechanism and Steric Limitations. The transition state for the reaction of **1** with one molecule of but-2-yne was determined by DFT calculations. The initial solid-state geometry of **1** with one but-2-yne molecule added in the equatorial plane (the plane perpendicular to the Cg(1)−Ti−Cg(2) angle and bisecting it) from the open shell side was optimized to a first-order saddle point. The transition-state geometry (Figure 11) is characterized by the triple bond prolongation to 1.39 Å and its π-mode binding to the titanium atom resembling the well-known structure of titanocene−bis(trimethylsilyl)ethyne complexes.[22]

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4b,e,g,m

	4b	**4e**	**4g**	**4m**
Bond Lengths (A)				
Ti−Cg(1)^a	2.1080(8)	2.1005(9)	2.1155(9)	2.1055(19)
Ti−Cg(2)^a	2.1334(8)	2.1145(9)	2.1435(10)	2.124(2)
Ti−Cl	2.3267(5)	2.3354(6)	2.3442(6)	2.3573(12)
Ti−C(22)	2.2466(16)	2.212(2)	2.257(2)	2.200(5)
C(21)−C(22)	1.356(2)	1.358(3)	1.366(3)	1.526(8)
C(6)−C(21)	1.521(2)	1.520(3)	1.520(3)	1.524(8)
Bond Angles (deg)				
Cg(1)−Ti−Cg(2)	135.94(3)	138.54(4)	134.88(4)	138.95((8)
Cg(1)−Ti−C(22)	100.28(5)	98.35(6)	101.36(6)	99.08(14)
Cg(2)−Ti−C(22)	107.37(5)	104.08(6)	106.39(6)	105.53(14)
Cg(1)−Ti−Cl	104.60(2)	105.68(3)	104.19(3)	106.19(6)
Cg(2)−Ti−Cl	105.74(2)	106.53(3)	106.02(4)	105.69(6)
Cl−Ti−C(22)	96.13(5)	95.01(6)	98.47(5)	91.02(15)
Ti−C(22)−C(21)	116.77(12)	121.38(15)	116.26(14)	112.9(3)
C(22)−C(21)−C(6)	120.24(15)	116.43(17)	120.79(18)	109.0(4)
Dihedral Angles (deg)				
φ^b	43.66(7)	40.81(10)	44.19(7)	41.64(12)
τ^c	6.3(2)	10.2(2)	11.9(2)	
ω^d	13.9(3)	8.9(3)	23.3(3)	

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(11−15) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares planes of cyclopentadienyl rings. [c] Dihedral angle Ti−C(22)−C(21)−C(6). [d] Dihedral angle involving C(21) and C(22) and attached atoms (C or Si) of their substituents.

The internal carbon atom of the arising tether is weakly bonded to the methylene carbon atom (C(1)−C(2) = 1.62 Å), and its bond to the titanium atom is longer than that of the terminal tether atom (Ti−C(2) = 2.36 Å versus Ti−C(3) = 2.17 Å). The imaginary frequency devised for the transition state breaks the Ti−C(2) bond and shortens the C(1)−C(2) and the C(2)−C(3) bonds, as expected for **3j** (see the corresponding bond lengths for **3a−g** in Table 2).

Theoretical investigations have also showed that the molecule constructed by insertion of two molecules of hex-3-yne into **1** (**2a**) is stable and its geometry is very similar to that of **2** (see the Supporting Information). Since the above experiments proved that compound **2** is formed via the intermediate compound **3j** and since compound **3i** was the sole product obtained with a large excess of hex-3-yne, it has to be assumed that it is steric congestion due to the presence of substituents larger than the methyl that does not allow an effective coordination of the second molecule of the respective alkyne to **3a−i** in a step which should precede its insertion. The reluctance of **3m** to insert another molecule of ethene is due to the lower reactivity of ethene compared to that of but-2-yne

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(21) (a) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457–466. (b) Lukešová, L.; Gyepes, R.; Pinkas, J.; Horáček, M.; Kubišta, J.; Čejka, J.; Mach, K. *Collect. Czech. Chem. Commun.* **2005**, *70*, 1589–1603.

(22) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A *Organometallics* **2003**, *22*, 884–900.

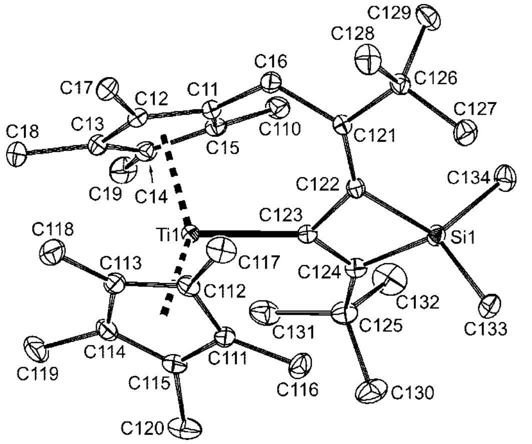

Figure 9. PLATON[30] drawing of **3l** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

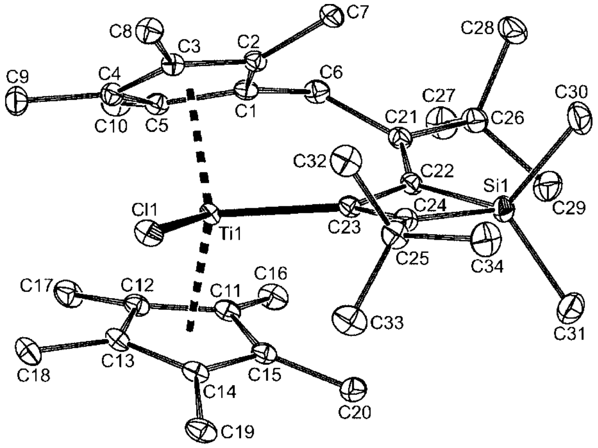

Figure 10. PLATON[30] drawing of **4l** at the 30% probability level with the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

and to the better stability of the propane-1,3-diyl tether compared to that of the longer pentane-1,5-diyl tether.

Conclusions

The singly tucked-in permethyltitanocene **1** rapidly inserts internal alkynes with not extremely bulky substituents into its highly reactive titanium−methylene bond to give the new class of thermally robust Ti(III) propenyl-tethered derivatives **3a**−**j**. Among them, only **3j** is able to insert another molecule of an alkyne, but-2-yne, to give the pentadienyl-tethered compound **2**. The reluctance of **3a**−**i** to insert the respective alkyne is due to insufficient coordination space at the titanium atom. The DFT calculation identified the transition state for formation of **3j** as arising from *π*-coordination of the alkyne in a pseudoequatorial plane. The mode of insertion of unsymmetrical alkynes is determined by the polarity of the $Ti^{\delta+}-C^{\delta-}R^1=$ bond as well as by steric congestion, and the high regioselectivity of the insertion is rather surprising. Thus, the electron-withdrawing groups preferably reside on this carbon (Ph, alkynyl, $SiMe_3$), whereas electron-donating alkyl groups (Me, *t*-Bu) occupy the other, more positive carbon atom of the double bond. In this respect, the electronic effects of the phenyl and trimethylsilyl groups should be similar, because only in the compound derived from phenyl(trimethylsilyl)ethyne were both isomers (**3c**, **3c′**) established in comparable abundance. Nonetheless, steric demands can also play an important role, as exemplified by the reluctance of **1** to react with sterically hindered alkynes or with the free triple bond of **3d**,**e**. The dialkynyldimethylsilanes react with **1** by both triple bonds; however, this occurs with the formation of a silacyclobutene moiety that has been encountered in similar titanocene and zirconocene systems.[11−13] Among a number of olefins only ethene underwent the insertion to give the propane-1,3-diyl tethered permethyltitanocene **3m**. An easy and nearly quantitative chlorination of paramagnetic compounds **3** affords diamagnetic compounds **4**, which are suitable for structure determination with NMR methods. Both series of

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 3k[a], 3l[a], and 4l[b]

	3k	**3l**	**4l**
	Bond Lengths (A)		
Ti(1)−Cg(11)[c]	2.0413(9)	2.0463(10)	2.1108(7)
Ti(1)−-Cg(12)[c]	2.0648(10)	2.0847(11)	2.1539(6)
Ti(1)−C(123)	2.1660(17)	2.180(2)	2.2012(13)
C(122)−C(123)	1.523(2)	1.518(3)	1.5281(18)
C(123)−C(124)	1.386(2)	1.376(3)	1.3876(18)
C(124)−Si(11)	1.856(2)	1.849(2)	1.8473(15)
C(122)−Si(11)	1.8932(18)	1.884(2)	1.8757(14)
C(121)−C(122)	1.348(3)	1.345(3)	1.3487(19)
C(121)−C(16)	1.537(3)	1.531(3)	1.522(2)
	Bond Angles (deg)		
Cg(11)−Ti(1)−Cg(12)	145.85((4)	143.17(4)	137.50(2)
Cg(11)−Ti(1)−C(123)	103.34(5)	102.24(6)	98.07(4)
Cg(12)−Ti(1)−C(123)	109.36(5)	110.37(6)	106.17(4)
Ti(1)−C(123)−C(122)	114.38(11)	118.49(13)	119.40(9)
Ti(1)−C(123)−C(124)	141.61(14)	138.42(16)	137.89(10)
C(122)−C(123)−C(124)	103.92(15)	103.05(17)	102.68(11)
C(123)−C(124)−Si(11)	92.66(12)	93.46(14)	93.41(9)
C(123)−C(122)−Si(11)	87.02(11)	87.69(12)	87.90(8)
C(122)−Si(11)−C(124)	75.37(8)	74.80(9)	75.46(6)
C(16)−C(121)−C(122)	125.92(17)	124.40(18)	124.42(12)
C(122)−C(121)−C(126)	120.05(14)	122.91(18)	122.47(13)
	Dihedral Angles (deg)		
C(122)−C(123)−C(124)−C(125)	166.47(17)	169.9(2)	171.80(17)
C(126)−C(121)−C(122)−Si(11)	29.7(3)	28.4(3)	25.0(2)
φ[d]	33.26(10)	35.89(11)	45.03(4)
τ[e]	28.45(11)	28.95(12)	31.53(4)
ω[f]	13.48(14)	11.26(15)	13.68(9)

[a] Two independent molecules in the unit cell differ slightly. The data for molecule 1 are listed only. Atoms for molecule 1 are numbered with prefix 1 (otherwise equally as for **4l**). [b] Additional data for **4l**: Ti−Cl = 2.3429(4) Å; Cl−Ti−C(23) = 103.92(4)°; Cg(1)−Ti−Cl = 104.06(2)°; Cg(2)−Ti−Cl = 103.27(2)°. [c] Cg(11) and Cg(12) are centroids of the C(11−15) and C(111−115) cyclopentadienyl rings, respectively. [d] Dihedral angle between the least-squares planes of cyclopentadienyl rings. [e] Dihedral angle between the least-squares planes of cyclopentadienyl ring C(1−5) and the silacyclobutene ring. [f] Dihedral angle between the least-squares planes of cyclopentadienyl ring C(111−115) and the silacyclobutene ring.

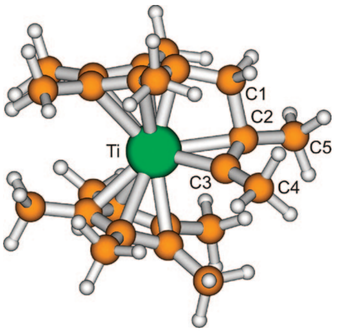

Figure 11. Transition state for the formation of **3j**. Calculated distances (Å): Ti−C(2) = 2.36, Ti−C(3) = 2.17, C(1)−C(2) = 1.62, C(2)−C(3) = 1.39, C(2)−C(5) = 1.53, C(3)−C(4) = 1.50.

Table 5. Crystallographic Data and Data Collection and Structure Refinement Details for 3a−g,k,l and 4b,e,g,l,m

	3a	**3b**	**3c**	**3d**	**3e**
formula	$C_{34}H_{39}Ti$	$C_{26}H_{41}SiTi$	$C_{31}H_{43}SiTi$	$C_{32}H_{47}Ti$	$C_{30}H_{47}Si_2Ti$
mol wt	495.55	429.58	491.64	479.60	511.76
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	10.0271(3)	34.8395(14)	8.6571(2)	8.8960(4)	13.7810(2)
b (Å)	13.3244(4)	8.5922(3)	14.2383(3)	15.2670(8)	12.3880(2)
c (Å)	20.5151(5)	20.4083(8)	14.2383(3)	15.2670(8)	18.3740(4)
α (deg)	90	90	99.8037(10)	92.443(2)	90
β (deg)	95.788(3)	125.7742(15)	90.9041(13)	105.854(3)	105.5660(10)
γ (deg)	90	90	103.7740(12)	111.242(3)	90
V (Å^3)	2726.95(13)	4956.5(3)	1359.02(6)	1465.42(12)	3021.74(9)
Z	4	8	2	2	4
D_{calcd} (g cm^{-3})	1.207	1.151	1.201	1.087	1.125
μ (mm^{-1})	0.334	0.403	0.376	0.308	0.378
color	reddish brown	brown	brown	reddish brown	red
cryst size (mm^3)	0.4 × 0.2 × 0.1	0.5 × 0.4 × 0.3	0.23 × 0.45 × 0.58	0.18 × 0.50 × 0.75	0.2 × 0.2 × 0.5
T (K)	180(2)	150(2)	150(2)	293(2)	150(2)
θ_{min}, θ_{max} (deg)	2.55, 27.10	2.00, 26.02	1.5, 27.6	3.10, 25.12	1.5, 27.5
range of h	−12 to +12	−42 to +42	−11 to +11	−10 to +10	−17 to +17
range of k	−17 to +17	−10 to +10	−14 to +14	−14 to +14	−16 to +16
range of l	−26 to +26	−25 to +25	−18 to +18	−18 to +18	−23 to +23
no. of rflns collected	23 547	28 513	22 685	16 077	51 240
no. of unique rflns	6011	4861	6236	5129	6919
F(000)	1060	1864	530	522	1108
no. of params	472	275	310	328	321
$R(F)$, $R_w(F^2)$ (all data) (%)	9.25, 8.97	5.35, 13.88	4.36, 9.31	8.61, 24.97	5.58, 10.18
GOF(F^2) (all data)	0.964	1.047	1.02	1.122	1.056
$R(F)$, $R_w(F^2)$ ($I > 2\sigma(I)$)	4.44, 7.60	4.96, 13.54	3.53, 8.82	7.56, 24.22	3.86, 9.32
$\Delta\rho$ (e Å$^{\prime -3}$)	0.22, −0.30	0.957, −0.566	0.36, −0.29	0.366, −0.353	0.25, −0.353

	3f	**3g**	**3k**	**3l**
formula	$C_{30}H_{45}Ti$	$C_{30}H_{49}Si_2Ti$	$C_{32}H_{53}Si_3Ti$	$C_{34}H_{53}SiTi$
mol wt	453.56	513.77	569.91	537.75
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic
space group	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)
a (Å)	14.9530(7)	9.0306(2)	19.3155(2)	29.3847(2)
b (Å)	17.0466(4)	11.9583(3)	12.0150(3)	11.9628(1)
c (Å)	21.4640(9)	14.7172(2)	28.9179(5)	18.7935(3)
α (deg)	90	89.3701(13)	90	90
β (deg)	90	82.0966(13)	90	108.4411(12)
γ (deg)	90	71.3318(10)	90	90
V (Å^3)	5471.1(4)	1490.48(5)	6711.1(2)	6267.11(12)
Z	8	2	8	8
D_{calcd} (g cm^{-3})	1.101	1.145	1.128	1.140
μ (mm^{-1})	0.327	0.383	0.380	0.331
color	dark red	red	green	green
cryst size (mm^3)	0.9 × 0.5 × 0.1	0.5 × 0.5 × 0.35	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.2
T (K)	293(2)	150(2)	150(2)	150(2)
θ_{min}, θ_{max} (deg)	3.12, 27.48	1.40, 27.46	1.41, 27.50	1.46, 27.58
range of h	−19 to +19	−11 to +11	−24 to +25	−38 to +38
range of k	−22 to +22	−15 to +15	−15 to +15	−15 to +15
range of l	−27 to +27	−18 to +19	−37 to +37	−24 to +24
no. of rflns collected	37 907	28 408	58 772	127 410
no. of unique rflns	6260	6803	14 750	14 392
F(000)	1976	558	2472	2344
no. of params	291	321	700	675
$R(F)$, $R_w(F^2)$ (all data) (%)	15.40, 18.83	4.0, 8.74	3.48, 7.85	6.39, 12.47
GOF(F^2) (all data)	1.022	1.025	1.037	1.063
$R(F)$, $R_w(F^2)$ ($I > 2\sigma(I)$)	6.74, 15.21	3.31, 8.26	3.07, 7.52	4.86, 11.69
$\Delta\rho$ (e Å$^{\prime -3}$)	0.445, −0.434	0.322, −0.338	0.251, −0.294	0.718, −0.367

	4b	**4e**	**4g**	**4l**	**4m**
formula	$C_{26}H_{41}ClSiTi$	$C_{30}H_{47}ClSi_2Ti$	$C_{30}H_{49}ClSi_2Ti$	$C_{34}H_{53}ClSiTi$	$C_{22}H_{33}ClTi$
mol wt	465.03	547.21	549.22	573.20	380.83
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	tetragonal
space group	$P2_12_12_1$ (No. 19)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{4}$ (No. 81)
a (Å)	10.4972(1)	22.1646(8)	8.6384(3)	31.7739(5)	15.3776(4)
b (Å)	11.3834(2)	18.0672(7)	11.4893(2)	20.4057(3)	15.3776(4)
c (Å)	20.9230(3)	15.7913(3)	15.6002(4)	11.1870(1)	8.3838(2)
α (deg)	90	90	78.9559(16)	90	90
β (deg)	90	97.899(2)	77.8493(14)	109.5524(9)	90
γ (deg)	90	90	86.9128(16)	90	90
V (Å^3)	2500.17(6)	6263.7(4)	1485.44(7)	6835.04(16)	1982.52(9)
Z	4	8	2	8	4
D_{calcd} (g cm^{-3})	1.235	1.161	1.228	1.114	1.276

Table 5. Continued

	4b	**4e**	**4g**	**4l**	**4m**
μ (mm^{-1})	0.508	0.383	0.476	0.383	0.567
color	dark red	dark red	brown	brown	brown
cryst size (mm^3)	0.5 × 0.5 × 0.3	0.5 × 0.35 × 0.2	0.5 × 0.45 × 0.25	0.6 × 0.5 × 0.25	0.5 × 0.5 × 0.3
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
$\theta_{\min}$, $\theta_{\max}$ (deg)	1.95, 27.48	1.87, 26.03	2.05, 27.47	1.36, 27.50	1.87, 27.13
range of h	−13 to +13	−27 to +27	−11 to +11	−41 to +41	−19 to +19
range of k	−14 to +14	−22 to +19	−14 to +14	−26 to +26	−19 to +19
range of l	−27 to +27	−19 to +19	−20 to +20	−14 to +14	−10 to +10
no. of rflns collected	36 612	30 206	26 429	64 166	31 026
no. of unique rflns	5736	6113	6779	7856	4359
F(000)	1000	2352	592	2480	816
no. of params	283	330	338	359	227
$R(F)$, $R_w(F^2)$ (all data) (%)	3.00, 7.25	5.13, 10.64	6.13, 10.40	4.02, 9.03	5.18, 15.17
GOF(F^2) (all data)	1.051	1.062	1.022	1.051	1.120
$R(F)$, $R_w(F^2)$ ($I > 2\sigma(I)$)	2.78, 7.10	3.88, 9.52	4.10, 9.37	3.20, 8.58	5.10, 15.10
$\Delta\rho$ (e Å$'^{-3}$)	0.251, −0.228	0.491, −0.369	0.345, −0.293	0.347, −0.276	1.019, −0.404

compounds have a high potential for further application in organometallic synthesis and catalysis: e.g., via formation of zwitterionic complexes with strong Lewis acids.

Experimental Section

General Considerations. Synthesis of **1** and its reactions with internal acetylenes and olefins were carried out under vacuum on a vacuum line in sealed all-glass devices equipped with breakable seals or under an argon atmosphere. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to the residual solvent signal (δ_H 7.15) and to the solvent resonance (δ_C 128.0). The δ_{Si} values are related to tetramethylsilane. The NOESY 1D experiment was performed using a mixing time of 500 ms. 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 7% and by important peaks of lower intensity. Crystals for EI-MS measurements and melting point determinations were placed in glass capillaries, and KBr pellets were prepared in a Labmaster 130 (mBraun) glovebox under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm) and sealed with flame. IR spectra were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400−4000 cm^{-1}. X-band EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany). g values were determined by using an Mn^{2+} standard at $g = 1.9860$ ($M_I = -{}^1/_2$ line). An STT-3 variable-temperature unit was used for measurements in the range −140 ± 25 °C. UV−near-IR spectra in the range 300−1000 nm were measured on a Varian Cary 17D spectrometer in all-sealed quartz cells (Hellma).

Chemicals. The solvents tetrahydrofuran (THF), hexane, and toluene were dried by refluxing over $LiAlH_4$ and stored as solutions of green dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4C_5H_4)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$.[23] C_6D_6 (99.5% D) was degassed, distilled on a vacuum line into a storage ampule containing dimeric titanocene, and stored as its solution. The alkynes but-2-yne, hex-3-yne, 1-(trimethylsilyl)prop-1-yne, 1-phenylprop-1-yne, phenyl(trimethylsilyl)ethyne, bis(trimethylsilyl)ethyne, and *tert*-butyl(trimethylsilyl)ethyne and olefins *cis*-/*trans*-but-2-ene, but-1-ene, hex-1-ene, *tert*-butylethene, and cyclopentene (all Aldrich) were degassed by freeze/thaw cycles and purified by dissolving the green dimeric titanocene until its solution remained green. Then the reagents were distilled off in vacuum systems. The solid diynes $t\text{-BuC}{\equiv}\text{CC}{\equiv}\text{C-}t\text{-Bu}$ and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (Aldrich) were degassed under vacuum. The diynes $Me_2Si(C{\equiv}C\text{-}t\text{-Bu})_2$ and $Me_2Si(C{\equiv}CSiMe_3)_2$ were prepared and used as reported elsewhere.[12] Head-to-tail dimers of 1-pentyne, (trimethylsilyl)ethyne, and *tert*-butylethyne ($RC{\equiv}CC(R){=}CH_2$; R = Pr, $SiMe_3$, t-Bu) were obtained using Ti catalysts.[24] Buta-1,3-diene of purity for Ti-catalyzed cyclotrimerization[25] and ethene purified by reaction with $[Ti(\eta^5\text{-}C_5Me_4SiMe_3)_2]$[26] were used. $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ and magnesium (turnings for Grignard reaction) were purchased from Aldrich and used as such after degassing. Methyllithium (LiMe) 1.6 M in diethyl ether (Aldrich) was degassed and distributed in sealed ampules. The singly tucked-in permethyltitanocene $[Ti^{III}\{\eta^5\text{:}\eta^1\text{-}C_5Me_4(CH_2)\}(\eta^5\text{-}C_5Me_5)]$ (**1**) was prepared from $[TiCl_2(\eta^5\text{-}C_5Me_5)_2]$ via $[TiCl(\eta^5\text{-}C_5Me_5)_2]$ and $[TiMe(\eta^5\text{-}C_5Me_5)_2]$ by thermolysis of the latter at 110 °C for 3 h (see the Supporting Information).

Preparation of 2 from 1. Compound **1** (0.50 g, 1.57 mmol) was dissolved in hexane (20 mL) and the solution mixed with but-2-yne (1.0 mL, 8.0 mmol) and stirred at room temperature. The initial purple color of **1** turned rapidly to ocher-brown and finally to khaki-green. After 3 h all volatiles were evaporated under vacuum, and a dark green residue was extracted with hexane (10 mL). The solution was concentrated to ca. 5 mL and left to crystallize in a freezer (−28 °C). Green crystalline product was separated and dried under vacuum. Yield: 0.57 g (86%). The product gave EI-MS, IR, EPR and UV−vis spectra identical with those reported for **2**.[9]

Preparation of Compounds 3a−g. Compound **1** (0.50 g, 1.57 mmol) was dissolved in hexane (20 mL), and the solution was mixed with the hexane solution of an internal alkyne (2−6 mmol in 15 mL). The solution was stirred at room temperature until the color changed to brown (1−3 h), and the stirring was continued for another such period (for **3g** see below). All volatiles were evaporated under vacuum, and the residue was dissolved in a minimum amount of hexane. For nonvolatile alkynes excess alkyne was removed from the product by fractional crystallization at low temperature (**3a**,**c**−**g**). Compounds **3a**−**g** were obtained pure by recrystallization from hexane.

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Compound 3a. The above quantity of **1** was reacted with diphenylethyne (0.712 g, 4.0 mmol in 15 mL) to give reddish brown crystals. Yield 0.61 g (78%).

Data for **3a** are as follows. Mp: 155 °C. EI-MS (150 °C): *m*/*z* (relative abundance) 497 (18), 496 (45), 495 ($M^{\bullet+}$; 100), 494 (20), 493 (19), 492 (7), 491 (11), 481 (7), 480 ([M − Me]$^+$; 14), 483 (13), 465 ([M − 2 Me]$^+$; 9), 389 (8), 361 (9), 319 (8), 318 (20), 317 ([M − L]$^+$; 63), 316 (10), 315 (13), 313 (9), 181 (11), 178 (23). IR (KBr, cm^{-1}): 3060 (w), 3051 (w), 3001 (m), 2960 (s), 2936 (s), 2902 (vs), 2861 (s), 2722 (vw), 1590 (s), 1582 (vw), 1570 (vw), 1532 (w), 1481 (s), 1439 (s), 1378 (s), 1312 (vw), 1199 (w), 1070 (w), 1022 (m), 902 (vw), 886 (vw), 832 (w), 786 (m), 758 (m), 748 (w), 699 (vs), 549 (vw), 530 (w), 511 (vw), 446 (s), 422 (m). EPR (toluene, 23 °C): $g = 1.948$, $\Delta H = 19$ G. EPR (toluene, −140 °C): $g_1 = 1.9992$, $g_2 = 1.9820$, $g_3 = 1.863$, $g_{av} = 1.948$. UV−vis (toluene, nm): 370 (sh) ≫ 500 > 650 (sh). Anal. Calcd for $C_{34}H_{39}Ti$ (495.54): C, 82.41; H, 7.93. Found: C, 82.38; H, 7.95.

Compound 3b. Reaction between **1** and 1-(trimethylsilyl)propyne (0.5 g, 5.3 mmol) afforded brown crystals highly soluble in hexane upon cooling to solid CO_2 temperature. Yield: 0.37 g (55%).

Data for **3b** are as follows. Mp: 95 °C. EI-MS (90 °C): *m*/*z* (relative abundance) 431 (20), 430 (40), 429 ($M^{\bullet+}$; 87), 428 (25), 427 (36), 426 (24), 425 (51), 424 (12), 423 (16), 414 ([M − Me]$^+$; 14), 413 ([M − H − Me]$^+$; 19), 412 ([M − 2H − Me]$^+$; 22), 355 (9), 354 ([M − 2H − $SiMe_3$]$^+$; 18), 353 (11), 341 (9), 319 (19), 318 (53), 317 ([M − L]$^+$; 100), 316 (28), 315 (38), 314 (13), 313 (28), 312 (9), 311 (17), 182 ([M − L − C_5Me_5]$^+$; 19), 181 (34), 180 (22), 179 (17), 178 (28), 177 (18), 176 (13), 97 (41), 73 (46). IR (KBr, cm^{-1}): 2984 (sh), 2950 (s), 2901 (vs), 2858 (s), 2817 (m), 2720 (vw), 1613 (w), 1578 (vw), 1493 (m), 1434 (m, b), 1378 (s), 1240 (s), 1160 (vw), 1130 (vw), 1066 (vw), 1023 (m), 989 (vw), 970 (vw), 873 (s), 835 (vs), 769 (w), 751 (vw), 684 (w), 665 (vw), 621 (w), 566 (w), 514 (w), 449 (m), 414 (m). EPR spectrum (hexane, 22 °C): $g = 1.9625$, $\Delta H = 8.5$ G. UV−vis (hexane, nm): 480 > 610 (sh). Anal. Calcd for $C_{26}H_{41}SiTi$ (429.56): C, 72.70; H, 9.62. Found: C, 72.75; H, 9.58.

Compound 3c. Reaction of **1** with phenyl(trimethylsilyl)ethyne (0.5 g, 2.9 mmol) gave after evaporation of hexane a brown solid. This was dissolved in 7.0 mL of toluene and crystallized by cooling to −28 °C. A crop of brown crystals was recrystallized from toluene. Yield: 0.17 g (23%). The mother liquor did not afford more crystals and was further analyzed after chlorination with $PbCl_2$ (see below).

Data for **3c** are as follows. Mp: 140 °C. EI-MS (130 °C): *m*/*z* (relative abundance) 493 (11), 492 (23), 491 ($M^{\bullet+}$; 50), 489 (14), 476 ([M − Me]$^+$; 11), 475 ([M − HMe]$^+$; 10), 418 ([M − $SiMe_3$]$^+$; 6), 417 ([M − $SiHMe_3$]$^+$; 7), 400 (12), 319 (13), 318 (33), 317 ([M − L]$^+$; 100), 316 (17), 315 (19), 313 (9), 182 (11), 181 (17), 178 (12), 73 (36). IR (KBr, cm^{-1}): 3090 (vw), 3063 (w), 2976 (s, b), 2902 (vs), 2861 (s), 2972 (vw), 1614 (vw), 1593 (w), 1572 (vw), 1488 (m), 1471 (s), 1437 (s), 1421 (m), 1379 (s), 1288 (vw), 1255 (m), 1239 (s), 1199 (vw), 1073 (vw), 1023 (m), 1000 (vw), 985 (vw), 911 (vw), 879 (vs), 833 (vs), 769 (s), 757 (s), 715 (s), 702 (s), 679 (w), 667 (w), 625 (w), 565 (w), 466 (w), 436 (m), 412 (m). EPR (toluene, 23 °C): $g = 1.948$, $\Delta H = 21$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.982$, $g_3 = 1.861$, $g_{av} = 1.947$. UV−vis (toluene, nm): 370 (sh) ≫ 458 > 700 (sh). Anal. Calcd for $C_{31}H_{43}SiTi$ (491.63): C, 75.73; H, 8.82. Found: C, 75.70; H, 8.78.

Compound 3d. This compound was obtained from 2,2′,7,7′-tetramethyl-octa-3,5-diyne (0.49 g, 3.0 mmol) as brown crystals. Yield: 0.51 g (68%).

Data for **3d** are as follows. Mp: 105 °C. EI-MS (100 °C): *m*/*z* (relative abundance) 481 (18), 480 (47), 479 ($M^{\bullet+}$; 100), 478 (24), 477 (28), 476 (7), 475 (9), 465 (7), 464 ([M − Me]$^+$; 16), 463 (7), 425 (10), 423 (14), 422 ([M − Bu]$^+$; 26), 421 (9), 420 (10), 408 (7), 407 ([M − Bu − Me]$^+$; 14), 318 (14), 317 ([M − L]$^+$; 47), 316 (8), 315 (9), 182 (7), 181 (15), 180 (10), 178 (10), 57 (22). IR (KBr, cm^{-1}): 2962 (vs), 2904 (vs), 2864 (s), 2721 (vw), 2187 (vw), 2153 (w), 1508 (w), 1494 (w), 1475 (s), 1437 (s, b), 1377 (vs), 1357 (s), 1295 (vw), 1264 (s), 1232 (m), 1206 (s), 1162 (vw), 1097 (m), 1079 (w), 1024 (s), 954 (vw), 923 (vw), 869 (vw), 825 (w), 802 (vw), 752 (w), 711 (w), 659 (vw), 615 (w), 529 (w), 496 (w), 458 (s), 414 (s). EPR (toluene, 23 °C): $g = 1.949$, $\Delta H = 20$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.983$, $g_3 = 1.870$, $g_{av} = 1.950$. UV−vis (toluene, nm): 438 ≫ 610 (sh). Anal. Calcd for $C_{32}H_{47}Ti$ (479.59): C, 80.14; H, 9.88. Found: C, 80.08; H, 9.83.

Compound 3e. This compound was obtained from 1,4-bis(trimethylsilyl)buta-1,3-diyne) (0.39 g, 2.0 mmol) as red crystals. Yield: 0.69 g (86%).

Data for **3e** are as follows. Mp: 83 °C. EI-MS (90 °C): *m*/*z* (relative abundance) 513 (15), 512 (28), 511 ($M^{\bullet+}$; 53), 510 (14), 509 (15), 496 ([M − Me]$^+$; 5), 438 ([M − $SiMe_3$]$^+$; 9), 423 ([M − $SiMe_3$ − Me]]$^+$; 4), 319 (23), 318 (68), 317 ([M − L]$^+$; 100), 316 (32), 315 (33), 313 (13), 200 (12), 181 (20), 180 (11), 179 (9), 178 (12), 73 (32). IR (KBr, cm^{-1}): 2954 (s), 2902 (s), 2863 (m, sh), 2722 (vw), 2150 (vw), 2079 (vs), 1488 (w), 1441 (m), 1407 (w), 1380 (m), 1245 (s), 1163 (vw), 1077 (m), 1052 (w), 856 (vs), 840 (vs), 754 (s), 694 (w), 676 (m), 651 (w), 620 (vw), 616 (vw), 498 (w), 449 (m), 424 (m). EPR (toluene, 23 °C): $g = 1.946$, $\Delta H = 28$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.983$, $g_3 = 1.865$, $g_{av} = 1.949$. UV−vis (toluene, nm): 500 > 665 (sh). Anal. Calcd for $C_{30}H_{47}Si_2Ti$ (511.74): C, 70.41; H, 9.26. Found: C, 70.46; H, 9.29.

Compound 3f. This compound was prepared from 2,4-dipropylbut-1-en-3-yne (head-to-tail dimer of 1-pentyne) (0.68 g, 5.0 mmol) to give brown crystals. Yield: 0.61 g (86%).

Data for **3f** are as follows. Mp: 110−112 °C. EI-MS (110 °C): *m*/*z* (relative abundance) 455 (12), 454 (30), 453 ($M^{\bullet+}$; 45), 452 (12), 451 (16), 449 (15), 440 (10), 439 (23), 438 ([M − Me]$^+$; 58), 437 (17), 436 (18), 319 (10), 318 (35), 317 ([M − L]$^+$; 100), 316 (19), 315 (23), 314 (9), 313 (19), 311 (13), 182 (14), 181 (25), 180 (17), 179 (11), 178 (17), 177 (13), 176 (8), 119 (7), 41 (13). IR (KBr, cm^{-1}): 3054 (w), 2953 (vs), 2897 (s), 2866 (s), 2721 (vw), 1604 (m), 1532 (m), 1492 (w), 1453 (s, b), 1376 (s), 1307 (vw), 1250 (vw), 1211 (vw), 1163 (vw), 1071 (vw), 1023 (m), 981 (vw), 907 (vw), 893 (vw), 855 (s), 739 (vw), 710 (w), 667 (vw), 596 (vw), 563 (w), 520 (vw), 507 (vw), 451 (m), 433 (m). EPR (toluene, 23 °C): $g = 1.952$, $\Delta H = 12$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.982$, $g_3 = 1.881$, $g_{av} = 1.954$. UV−vis (toluene, nm): 495 > 630 (sh). Anal. Calcd for $C_{30}H_{45}Ti$ (453.55): C, 79.44; H, 10.00. Found: C, 79.50; H, 9.95.

Compound 3g. This compound was obtained from 2,4-bis(trimethylsilyl)but-1-ene-3-yne (head-to-tail dimer of (trimethylsilyl) ethyne) (1.0 mL, 5.0 mmol). The reaction required heating to 60 °C for 3 h. Brown crystals were obtained from hexane. Yield: 0.68 g (85%).

Data for **3g** are as follows. Mp: 135 °C. EI-MS (130 °C): *m*/*z* (relative abundance) 514 (15), 513 ($M^{\bullet+}$; 22), 512 (12), 511 (19), 498 ([M − Me]$^+$; 13), 440 ([M − $SiMe_3$]$^+$; 7), 319 (30), 318 (60), 317 ([M − L]$^+$; 100), 316 (49), 315 (55), 314 (17), 313 (42), 312 (13), 311 (21), 196 ($L^{\bullet+}$; 47), 183 (12), 182 (32), 181 ([L − Me]$^+$; 90), 180 (19), 179 (13), 178 (22), 177 (14), 156 (19), 155 (85), 119 (9), 108 (30), 97 (11), 83 (11), 74 (10), 73 (92), 45 (21), 43 (12). IR (KBr, cm^{-1}): 3038 (vw), 3015 (vw), 2958 (s), 2904 (vs), 2858 (s), 2725 (vw), 1600 (w, b), 1486 (m), 1433 (s, b), 1378 (s), 1247 (s), 1166 (vw), 1149 (vw), 1067 (w), 1023 (m), 926 (w), 892 (w), 838 (vs), 807 (m), 755 (m), 725 (w), 692 (w), 620 (w), 566 (m), 516 (w), 474 (w), 430 (s). EPR (toluene, 23 °C): $g = 1.952$, $\Delta H = 15$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.982$, $g_3 = 1.874$, $g_{av} = 1.952$. UV−vis (toluene, nm): 464 > ~600 (sh). Anal. Calcd for $C_{30}H_{49}Si_2Ti$ (513.75): C, 70.13; H, 9.61. Found: C, 70.06; H, 9.59.

Preparation of 3h. Compound **1** (0.50 g, 1.57 mmol) was reacted with 1-phenylprop-1-yne (0.26 g, 2.2 mmol) in 10 mL of hexane to give a brown solution showing EPR and UV−vis spectra which were attributable to **3h**. Since all attempts for the product crystallization gave only a brown wax, this was finally dried under vacuum and used for the preparation of its chloro derivative **4h**, which was characterized (see below).

Data for **3h** are as follows. EPR (hexane, 22 °C): $g = 1.954$, $\Delta H = 21$ G. UV−vis (hexane, nm): 485 ≫ 640 (sh).

Preparation of 3i. Compound **1** (0.50 g, 1.57 mmol) was reacted with hex-3-yne (0.4 g, 4.9 mmol) in 10 mL of hexane. The reaction was complete after 1 h to give an ocher solution which displayed EPR and UV−vis spectra attributable to **3i**. Evaporation of all volatiles yielded an ocher oil which did not crystallize. The oily product was used for the preparation of **4i**, which was characterized (see below).

Data for **3i** are as follows. EPR (hexane, 22 °C): $g = 1.956$, $\Delta H = 14$ G. UV−vis (hexane, nm): 495 (sh) > 580 (sh).

Preparation of 3j. A solution of **1** (0.50 g, 1.57 mmol) in hexane (10 mL) was precooled to ca. −20 °C, and but-2-yne (0.14 mL, 1.75 mmol) was rapidly condensed from the gas phase into the stirred solution. The purple color changed immediately to brownish yellow. After the mixture was stirred for 30 s, all volatiles were distilled off by condensation to liquid nitrogen temperature. A brown residue was dissolved in a minimum amount of hexane and crystallized at −28 °C. The first crop of crystals (0.14 g) was separated and discarded, as their greenish coloration suggested the presence of **2**. The mother liquor was concentrated and cooled in a freezer to give a brown fine polycrystalline material extremely soluble in hexane. After separation from mother liquor and drying under vacuum, a brown powder was obtained. Yield: 0.32 g (55%).

Data for **3j** are as follows. Mp: 105 °C. EI MS (100 °C): *m*/*z* (relative abundance, %) 373 (17), 372 (36), 371 ($M^{\bullet+}$; 74), 370 (29), 369 (33), 368 (37), 367 ($[M - 2\,H_2]^+$; 100), 366 (23), 365 (32), 364 (8), 363 (15), 356 (13), 355 (25), 354 ($[M - Me - H_2]^+$; 45), 353 (17), 352 (15), 342 (16), 341 ($[M - 2\,Me]^+$; 24), 340 (10), 339 ($[M - 2\,Me - H_2]^+$; 12), 318 (11), 317 ($[M - L]^+$; 27), 316 (10), 315 (13), 314 (10), 313 (18), 254 (12), 202 (32), 201 (12), 200 (19), 199 (16), 195 (15), 183 (21), 182 (21), 181 (39), 180 (26), 179 (21), 178 (31), 177 (22), 176 (20), 175 (12), 167 (17), 166 (10), 165 (11), 164 (12), 163 (14), 152 (15), 151 (11), 150 (14), 135 (21), 133 (15), 120 (16), 119 (25), 105 (30), 93 (23), 91 (23), 79 (17), 77 (15). IR (KBr, cm^{-1}): 2972 (m), 2906 (vs), 2860 (s), 2720 (vw), 1543 (w), 1493 (m), 1445 (s, b), 1378 (vs), 1309 (vw), 1023 (m), 807 (w), 615 (vw), 565 (w), 450 (m), 427 (m). EPR (toluene, 22 °C): $g = 1.957$; $\Delta H = 11.6$ G. EPR (toluene, −140 °C): $g_1 = 2.000$; $g_2 = 1.982$; $g_3 = 1.894$; $g_{av} = 1.958$. UV−vis (toluene, nm): 475 (sh) > 630 (sh). Anal. Calcd for $C_{24}H_{35}Ti$ (371.39): C, 77.61; H, 9.50. Found: C, 77.66; H, 9.54.

Preparation of 3k. Compound **1** (0.50 g, 1.57 mmol) was reacted with $Me_2Si(C{\equiv}CSiMe_3)_2$ (0.43 g, 1.7 mmol) in 10 mL of hexane. The reaction was complete after 30 min at 60 °C. A dark yellow product crystallized out from a concentrated solution. Recrystallization from hexane afforded dark yellow crystals. Yield: 0.83 g (93%).

Data for **3k** are as follows. Mp: 90−95 °C. EI-MS (90 °C): *m*/*z* (relative abundance) 569 ($M^{\bullet+}$; 4), 319 (13), 318 (37), 317 ($[M - L]^+$; 92), 316 (29), 315 (44), 314 (17), 313 (38), 312 (11), 311 (19), 253 (19), 252 ($L^{\cdot+}$; 67), 239 (33), 238 (64), 237 ($[L - Me]^+$; 100), 181 (16), 180 (9), 179 (14), 178 (15), 177 (13), 155 (12), 151 (10), 111 (54), 97 (18), 83 (13), 73 (69). IR (KBr, cm^{-1}): 2984 (m, sh), 2950 (s), 2898 (s), 2856 (m, sh), 2794 (w), 2721 (vw), 1550 (w), 1487 (w), 1436 (m), 1401 (w), 1244 (s), 1023 (w), 991 (s), 894 (s), 857 (vs), 834 (vs), 767 (s), 747 (m), 685 (m), 632 (m), 607 (vw), 565 (w), 550 (vw), 458 (m), 436 (s). EPR (toluene, 23 °C): $g = 1.942$, $\Delta H = 41$ G. EPR (toluene, −140 °C): $g_1 = 1.998$, $g_2 = 1.980$, $g_3 = 1.842$, $g_{av} = 1.940$. UV−vis (toluene, nm): 460 > 620 (sh). Anal. Calcd for $C_{32}H_{53}Si_3Ti$ (569.89): C, 67.42; H, 9.37. Found: C, 67.40; H, 9.39.

Preparation of 3l. Compound **1** (0.50 g, 1.57 mmol) was reacted with $Me_2Si(C{\equiv}CCMe_3)_2$ (0.40 g, 1.8 mmol) after warming the reaction mixture to 60 °C for 1 h. After the concentrated solution was cooled to −28 °C, brownish yellow crystalline material was separated from a brown mother liquor. The product was recrystallized from hexane to give dark yellow crystals. Yield: 0.73 g (87%).

Data for **3l** are as follows. Mp: 100−102 °C. EI-MS (100 °C): *m*/*z* (relative abundance) 538 (6), 537 ($M^{\bullet+}$; 12), 522 ($[M - Me]^+$; 2), 480 ($[M - Bu]^+$; 2), 319 (29), 318 (77), 317 ($[M - L]^+$; 100), 316 (36), 315 (38), 313 (11), 181 (14), 180 (10), 178 (9), 73 (18), 57 (13). IR (KBr, cm^{-1}): 2953 (vs), 2901 (s), 2861 (m), 2798 (vw), 2720 (vw), 1589 (vw), 1514 (w), 1475 (m), 1460 (m), 1444 (m), 1377 (m), 1356 (m), 1286 (w), 1242 (m), 1192 (w), 1086 (w), 1073 (m), 1024 (w), 970 (vw), 952 (vw), 924 (vw), 836 (s), 814 (m), 775 (s), 764 (s), 697 (s), 614 (w), 579 (w), 496 (vw), 436 (m). EPR (toluene, 23 °C): $g = 1.952$, $\Delta H = 20$ G. EPR (toluene, −140 °C): $g_1 = 1.999$, $g_2 = 1.982$, $g_3 = 1.883$, $g_{av} = 1.954$. UV−vis (toluene, nm): 455 > 615 (sh). Anal. Calcd for $C_{34}H_{53}SiTi$ (537.74): C, 75.94; H, 9.93. Found: C, 75.90; H, 9.90.

Preparation of 3m. A 0.5 mL amount of liquid ethene was condensed at liquid nitrogen temperature and subsequently dissolved in a solution of **1** (1.1 g, 3.5 mmol) in 20 mL of hexane. After the mixture stood overnight at 20 °C, a clean brown solution was carefully evaporated, and the residue was dissolved in 5 mL of hexane. Cooling to −28 °C afforded a brown polycrystalline material, which was collected. A slow recrystallization yielded, in addition to a brown polycrystalline product, several red-brown prisms as a very minor component less soluble in hexane. Their analysis by X-ray diffraction indicated that the crystals contained two pairs of molecules of **1** and **3m** in the unit cell. Unfortunately, the molecules were heavily disordered, which did not allow us to determine the correct molecular parameters. The presence of **1** in these crystals was confirmed by a very weak shoulder at 3018 cm^{-1} and an absorption band of medium intensity at 430 cm^{-1} in their IR spectra. These bands were missing in IR spectra of the bulk of **3m**. Yield: 1.05 g (87%).

Data for **3m** are as follows. Mp: 80−82 °C. EI-MS (80 °C): *m*/*z* (relative abundance) 347 (11), 346 (22), 345 ($M^{\bullet+}$; 53), 344 (29), 343 (49), 342 (36), 341 ($[M - 2\,H_2]^+$; 100), 340 (32), 339 (73), 338 (14), 337 (18), 319 (11), 318 (27), 317 ($[M - C_2H_4]^+$; 67), 316 (26), 315 (26), 314 (11), 313 (24), 311 (16), 203 (16), 202 (10), 200 (13), 181 (27), 180 (18), 179 (19), 178 (27), 177 (22), 176 (15). EI-MS (15 eV, 70 °C): *m*/*z* (relative abundance) 347 (13), 346 (29), 345 ($M^{\bullet+}$; 100), 344 (10), 343 ($[M - H_2]^+$; 41), 342 (11), 341 ($[M - 2\,H_2]^+$; 23), 340 (7), 339 (13), 319 (7), 318 (18), 317 ($[M - C_2H_4]^+$; 63), 316 (14), 315 (10). IR (KBr, cm^{-1}): 2906 (vs), 2857 (s), 2809 (m), 2722 (vw), 1487 (m), 1442 (s, b), 1378 (vs), 1312 (vw), 1202 (vw), 1067 (vw), 1023 (m), 896 (vw), 849 (w), 805 (w), 755 (vw), 723 (w), 680 (vw), 617 (vw), 563 (w), 517 (vw), 466 (w), 442 (s). EPR (toluene, 23 °C): $g = 1.959$, $\Delta H = 19$ G. EPR (toluene, −140 °C): $g_1 = 2.000$, $g_2 = 1.983$, $g_3 = 1.897$, $g_{av} = 1.960$. UV−vis (toluene, nm): 325 (sh), 375 (sh) ≫ 444 > 560 (sh). Anal. Calcd for $C_{22}H_{33}Ti$ (345.35): C, 76.51; H, 9.63. Found: C, 76.48; H, 9.60.

Preparation of Chlorinated Compounds 4a−m. Pure crystalline products **3a**,**b**,**d**−**g**,**k**−**m** and crude products **3c**,**h**−**j** were dissolved in THF (10 mL), and the brown solutions were poured onto degassed powdery $PbCl_2$ (slightly more than $^1/_2$ molar equiv). After 15 min of vigorous stirring the solutions turned red and white $PbCl_2$ turned to black lead. THF was distilled off for another use, and the residues were extracted with toluene. The products were crystallized from concentrated toluene solution by cooling, and red crystalline products were dried under vacuum.

Preparation of 4a. Crystals of **3a** (0.21 g, 0.42 mmol) reacted with $PbCl_2$ (0.07 g, 0.25 mmol) to give a bright red polycrystalline powder. Yield: 0.21 g (94%).

Data for **4a** are as follows. Mp: 219 °C. ^1H NMR (C_6D_6): 1.66 (s, 15H, C_5Me_5);1.68, 1.87, 1.93, 2.63 (4 × s, 4 × 3H, C_5Me_4); 3.14, 3.44 (2 × d, 2 × $^2J_{HH}$ = 17.1 Hz, 2 × 1H, C(6)H_2); 6.81−7.08 (m, 8H, *Ph*); 7.10−7.14 (m, 2H, CH_{ortho}, C(22)*Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6): 11.58, 11.78 (C_5Me_4); 12.79 (C_5Me_5); 13.76, 14.54 (C_5Me_4); 37.77 (*C*(6)); 118.01, 121.05 (C_5Me_4; 124.01, 125.36, 126.12, 131.80 others are obscured by stronger solvent signal (*C*H, *Ph*); 125.14 (C_5Me_5); 128.69, 132.10, 138.76, 143.70, 149.60 (C_5Me_4 and C_{ipso} (*Ph*)); 157.35 (*C*(21)); 204.41 (*C*(22)). EI-MS (210 °C): *m/z* (relative abundance) 532 (21), 531 (26), 530 ($M^{\bullet+}$; 47), 529 (22), 494 ($[M - HCl]^+$; 9), 399 (13), 398 (42), 397 (39), 396 ($[M - C_5Me_4CH_2]^+$; 100), 395 (26), 394 (14), 220 (28), 219 (23), 218 ($[M - L - C_5Me_4CH_2]^+$; 76), 217 (29), 216 (24), 215 (13), 214 (8), 213 (23), 178 (21), 135 (15), 119 (17), 105 (12), 91 (10). IR (KBr, cm^{-1}): 3069 (w), 3048 (m), 3003 (s), 2946 (m), 2899 (vs), 2842 (m), 2717 (vw), 1938 (vw), 1878 (vw), 1808 (vw), 1589 (m), 1567 (vw), 1543 (vw), 1485 (s), 1437 (s), 1376 (s), 1311 (vw), 1243 (vw), 1193 (vw), 1152 (vw), 1071 (w), 1020 (m), 932 (vw), 888 (vw), 832 (vw), 783 (m), 762 (m), 746 (w), 700 (vs), 638 (vw), 579 (vw), 547 (vw), 531 (w), 499 (vw), 464 (w), 415 (s). UV−vis (toluene, nm): 465 > 540 (sh). Anal. Calcd for $C_{34}H_{39}ClTi$ (530.99): C, 76.91; H, 7.40. Found: C, 76.96; H, 7.36.

Preparation of 4b. Brown crystalline **3b** (0.25 g, 0.58 mmol) reacted with $PbCl_2$ (0.09 g, 0.32 mmol) to give bright red crystals. Yield: 0.20 g (75%).

Data for **4b** are as follows. Mp: 195 °C. ^1H NMR (C_6D_6): 0.40 (s, 9H, SiMe_3); 1.58, 1.92, 1.93, 2.37 (4 × s, 4 × 3H, C_5Me_4); 1.79 (s, 15H, C_5Me_5); 1.81 (d, $^4J_{HH}$ = 1.2 Hz, 3H, C(7)*Me*); 2.81 (d, $^2J_{HH}$ = 17.4 Hz, 1H, C(6)H_2); 2.93 (dq, $^2J_{HH}$ = 17.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C(6)H_2). $^{13}C\{^1H\}$ NMR (C_6D_6): 6.26 (SiMe_3); 10.68, 12.40 (C_5Me_4); 12.78 (C_5Me_5); 14.20, 15.52 (C_5Me_4); 24.53 (C(21)*Me*); 40.47 (*C*(6)); 116.21, 123.20, 127.05, 132.14, 134.36 (C_5Me_4); 123.90 (C_5Me_5); 157.39 (*C*(21)); 212.91 (*C*(22)). $^{29}Si\{^1H\}$ NMR (C_6D_6): −13.87 (*Si*Me_3). EI-MS (180 °C): *m/z* (relative abundance) 466 (15), 465 (14), 464 ($M^{\bullet+}$; 29), 451 (6), 449 ($[M - Me]^+$; 11), 428 ($[M - HCl]^+$; 5), 355 (10), 354 (34), 353 (27), 352 ($[M - L]^+$; 75), 351 (10), 350 (9), 332 (9), 331 (11), 330 ($[M - C_5Me_4CH_2]^+$; 20), 329 (16), 317 ($[M - Cl - L]^+$; 21), 221 (11), 220 (58), 219 (44), 218 ($[M - L - C_5Me_4CH_2]^+$; 100), 217 (52), 216 (33), 215 (16), 214 (9), 213 (26), 178 (9), 135 (8), 119 (18), 105 (9), 91 (7), 73 (25). IR (KBr, cm^{-1}): 2987 (m), 2946 (s), 2898 (vs), 2863 (s), 2818 (m), 2716 (vw), 1520 (w), 1502 (m), 1434 (m, b), 1376 (s), 1294 (vw), 1256 (m), 1239 (s), 1065 (vw), 1020 (m), 881 (s), 841 (vs), 757 (w), 733 (w), 672 (m), 621 (w), 596 (vw), 517 (w), 466 (vw), 429 (m). UV−vis (hexane, nm): 435 (sh) > 540 (sh). Anal. Calcd for $C_{26}H_{41}ClSiTi$ (465.01): C, 67.15; H, 8.89. Found: C, 67.20; H, 8.92.

Preparation of 4c/4c′. The mother liquor from **3c** was evaporated under vacuum, and the residue (0.54 g, 1.10 mmol) was dissolved in THF and this solution reacted with $PbCl_2$ (0.16 g, 0.57 mmol). A bright red waxy residue was obtained after evaporation of toluene. It turned into a polycrystalline solid after long evacuation. ^1H, ^{13}C, and ^{29}Si NMR spectra revealed that regioisomer **4c′** is contained in 85% abundance, whereas **4c** is a minor species (see Table 1). Yield: 0.53 g (93%).

Mp: 155 °C. Data for **4c** (15%) are as follows. ^1H NMR (C_6D_6): 0.10 (s, 9H, SiMe_3); 1.84 (s, 15H, C_5Me_5); 1.89, 1.97 (2 × s, 2 × 3H, C_5Me_4); 2.89, 3.16 (2 × d, 2 × $^2J_{HH}$ = 18.6 Hz, 2 × 1H, C(6)H_2); other signals were not detected due to overlapping by stronger signals of **4c′**. $^{13}C\{^1H\}$ NMR (C_6D_6): 6.43 (SiMe_3); 10.82, 12.53 (C_5Me_4); 12.89 (C_5Me_5); 14.46, 15.74 (C_5Me_4); 43.27 (*C*(6)); 119.11, 121.69 (C_5Me_4); 122.96 (C_5Me_5); 124.05 (C_5Me_4); 124.55, 126.67, 129.62 (*C*H, *Ph*); 130.85, 133.99 (C_5Me_4); 145.84 (C_{ipso} (*Ph*)); 161.03 (*C*(21)); 215.05 (*C*(22)). $^{29}Si\{^1H\}$ NMR (C_6D_6): −11.86 (*Si*Me_3). Data for **4c′** (85%) are as follows. ^1H NMR (C_6D_6): −0.08 (s, 9H, SiMe_3); 1.62 (s, 15H, C_5Me_5); 1.73, 1.77, 1.85, 2.62 (4 × s, 4 × 3H, C_5Me_4); 2.91, 3.25 (2 × d, 2 × $^2J_{HH}$ = 16.8 Hz, 2 × 1H, C(6)H_2); 6.88−7.22 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6): 1.92 (SiMe_3); 11.75, 11.99 (C_5Me_4); 12.71 (C_5Me_5); 13.20, 15.27 (C_5Me_4); 36.32 (*C*(6)); 118.60, 120.66, 124.20 (C_5Me_4); 124.55 (*C*H, *Ph*); 124.97 (C_5Me_5); 126.67 (*C*H, *Ph*); 128.99 (C_5Me_4); 129.62 (*C*H, *Ph*); 148.75, 153.56 (C_{ipso} (*Ph*) and C_5Me_4); 163.63 (*C*(21)); 221.96 (*C*(22)). $^{29}Si\{^1H\}$ NMR (C_6D_6): −12.32 (*Si*Me_3). EI-MS (200 °C): *m/z* (relative abundance) 528 (10), 527 (13), 526 ($M^{\bullet+}$; 16), 511 ($[M - Me]^+$; 5), 491 (7), 490 ($[M - HCl]^+$; 14), 453 ($[M - SiMe_3]^+$; 5), 418 ($[M - Cl - SiMe_3]^+$; 5), 392 ($[M - C_5Me_4CH_2]^+$; 11), 355 (11), 354 (40), 353 (31), 352 ($[M - L]^+$; 91), 351 (12), 350 (11), 317 ($[M - L - Cl]^+$; 6), 220 (41), 219 (30), 218 ($[M - L - C_5Me_4CH_2]^+$; 100), 217 (32), 216 (26), 215 (11), 214 (7), 213 (19), 119 (14), 73 (57). IR (KBr, cm^{-1}): 3069 (vw), 3047 (w), 2998 (m), 2947 (s), 2896 (vs), 2844 (m, sh), 2719 (vw), 1590 (w), 1567 (vw), 1495 (m), 1473 (w), 1435 (m), 1376 (m), 1254 (m), 1243 (s), 1073 (vw), 1024 (m), 921 (vw), 885 (w), 844 (vs), 835 (vs), 768 (m), 755 (m), 707 (s), 680 (vw), 647 (w), 506 (w), 416 (s). UV−vis (hexane, nm): 445 (sh) > 540 (sh). Anal. Calcd for $C_{31}H_{43}ClSiTi$ (527.08): C, 70.64; H, 8.22. Found: C, 70.70; H, 8.28.

Preparation of 4d. Compound **3d** (0.25 g, 0.52 mmol) reacted with $PbCl_2$ (0.09 g, 0.32 mmol) to give bright red crystals from hexane. Yield: 0.24 g (91%).

Data for **4d** are as follows. Mp: 180 °C. ^1H NMR (C_6D_6): 1.31 (s, 9H, ≡CCMe_3); 1.40 (s, 9H, C(21)CMe_3); 1.58, 1.81, 1.99, 2.49 (4 × s, 4 × 3H, C_5Me_4); 1.96 (s, 15H, C_5Me_5); 2.86, 3.12 (2 × d, 2 × $^2J_{HH}$ = 18.6 Hz, 2 × 1H, C(6)H_2). $^{13}C\{^1H\}$ NMR(C_6D_6): 10.77, 11.74 (C_5Me_4); 12.98 (C_5Me_5); 13.82, 14.36 (C_5Me_4); 29.14 (*C*Me_3); 29.78, 31.03 (2 × CMe_3); 32.61 (*C*Me_3); 37.97 (*C*(6)); 89.58 (C(22)*C*≡C); 113.02 (C≡*C*CMe_3); 114.73, 122.79 (C_5Me_4); 124.53 (C_5Me_5); 127.46, 132.52, 134.64 (C_5Me_4); 164.05 (*C*(21)); 178.45 (*C*(22)). EI-MS (170 °C): *m/z* (relative abundance) 517 (13), 516 (15), 515 (18), 514 ($M^{\bullet+}$; 27), 502 (9), 501 (16), 500 (14), 499 ($[M - Me]^+$; 32), 464 ($[M - Me - Cl]^+$; 11), 463 ($[M - Me - HCl]^+$; 12), 457 ($[M - Bu]^+$; (6), 382 (15), 381 (41), 380 (38), 379 ($[M - C_5Me_5]^+$; 83), 378 (15), 377 (14), 221 (13), 220 (40), 219 (33), 218 ($[M - L - C_5Me_4CH_2]^+$; 100), 217 (44), 216 (31), 215 (23), 214 (15), 213 (42), 135 (16), 119 (30), 57 (56). IR (KBr, cm^{-1}): 2963 (vs), 2901 (vs), 2861 (s), 2720 (vw), 1530 (w), 1501 (m), 1445 (s, b), 1384 (m), 1376 (vs), 1358 (s), 1266 (s), 1240 (m), 1205 (m), 1103 (vw), 1066 (vw), 1020 (m), 843 (w), 753 (vw), 617 (w), 536 (w), 440 (s). UV−vis (hexane, nm): 452 > 535 (sh). Anal. Calcd for $C_{32}H_{47}ClTi$ (515.04): C, 74.62; H, 9.20. Found: C, 74.58; H, 9.23.

Preparation of 4e. The above procedure using **3e** (0.33 g, 0.65 mmol) and $PbCl_2$ (0.10 g, 0.36 mmol) afforded bright red crystals. Yield: 0.22 g (62%).

Data for **4e** are as follows. Mp: 154 °C. ^1H NMR (C_6D_6): 0.28 (s, 9H, SiMe_3); 0.38 (s, 9H, SiMe_3); 1.54, 1.82, 1.95, 2.46 (4 × s, 4 × 3H, C_5Me_4); 1.94 (s, 15H, C_5Me_5); 2.78, 3.00 (2 × d, 2 × $^2J_{HH}$ = 18.6 Hz, 2 × 1H, C(6)H_2). $^{13}C\{^1H\}$ NMR (C_6D_6): −0.37, 0.19 (2 × SiMe_3); 10.71, 11.99 (C_5Me_4); 12.98 (C_5Me_5); 14.38, 14.87 (C_5Me_4); 35.31 (*C*(6)); 106.69, 115.60 (*C*≡*C*); 113.71, 124.82, 127.49, 134.97, 140.18 (C_5Me_4); 125.17 (C_5Me_5); 166.79 (*C*(21)); 195.11 (*C*(22)). ^{29}Si $\{^1H\}$(C_6D_6): − 21.12 (≡C*Si*Me_3), −11.81 (=C*Si*Me_3). EI-MS (140 °C): *m/z* (relative abundance) 549 (9), 548 (13), 547 (12), 546 ($M^{\bullet+}$; 22), 531 ($[M - Me]^+$; 12), 510 ($[M - HCl]^+$; 10), 495 ($[M - Me - HCl]^+$; 7), 473 ($[M - SiMe_3]^+$; 7), 414 (12), 413 (18), 412 (24), 411 ($[M - C_5Me_5]^+$; 23), 396 ($[M - Me - C_5Me_5]^+$; 7), 355 (8), 354 (27), 353 (22), 352 ($[M - L]^+$; 62), 317 ($[M - L - Cl]^+$; 9), 221 (8), 220 (38), 219 (29), 218 ($[M - L - C_5Me_4CH_2]^+$; 100), 217 (35), 216 (26), 215 (14), 214 (9), 213 (21), 135 (12), 119 (14), 73 (71). IR (KBr, cm^{-1}): 2989 (m, sh), 2954 (s), 2897 (s), 2823 (w, sh), 2720 (vw), 2162 (vw), 2084 (s), 1494 (m), 1444 (m), 1403 (w), 1377 (m), 1245 (s), 1081 (m), 1045 (w), 1022 (w), 912 (vw), 854 (vs, b), 756 (m), 692 (w), 675 (w), 647 (w), 618 (vw), 482 (w), 444 (m), 430 (m), 417 (m). UV−vis (toluene, nm): 452 > 530 (sh). Anal. Calcd for $\mathrm{C_{30}H_{47}ClSi_2Ti}$ (547.19): C, 65.85; H, 8.66. Found: C, 65.90; H, 8.62.

Preparation of 4f. Crystalline **3f** (0.32 g, 0.71 mmol) reacted with $\mathrm{PbCl_2}$ (0.11 g, 0.40 mmol) to give a red solution which after the usual workup yielded red crystals from hexane. Yield: 0.30 g (87%).

Data for **4f** are as follows. Mp: 135 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): 0.99 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, $\mathrm{CH_2CH_2}\mathit{Me}$); 1.05 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, $\mathrm{CH_2CH_2}\mathit{Me}$); 1.21−1.61 (m, 4H, 2 × $\mathrm{C}\mathit{H}_2\mathrm{Me}$); 1.73, 1.74, 1.78, 2.49 (4 × s, 4 × 3H, $\mathrm{C_5}\mathit{Me}_4$); 1.87 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 2.00−2.18 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Me}$); 2.33−2.52 partially overlapped by stronger methyl signal (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Me}$); 2.94, 3.02 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 17.4 Hz, 2 × 1H, $\mathrm{C(6)}\mathit{H}_2$); 4.35, 4.77 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 3.3 Hz, 2 × 1H, $=\mathrm{C}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): 11.14, 12.13 ($\mathrm{C_5}\mathit{Me}_4$); 12.76 ($\mathrm{C_5}\mathit{Me}_5$); 14.26, the fourth overlapped by stronger $\mathrm{C_5}\mathit{Me}_5$ signal ($\mathrm{C_5}\mathit{Me}_4$); 14.74, 14.77 (2 × $\mathrm{CH_2CH_2}\mathit{Me}$); 21.95, 23.82 (2 × $\mathrm{CH_2}\mathit{C}\mathrm{H_2Me}$); 34.96 ($C$(6)); 36.10, 41.08 (2 × $\mathit{C}\mathrm{H_2CH_2Me}$); 106.31 ($=\mathit{C}\mathrm{H_2}$); 118.62, 120.54 ($\mathit{C}_5\mathrm{Me_4}$); 124.50 ($\mathit{C}_5\mathrm{Me_5}$); 125.77, 130.05, 141.91 ($\mathit{C}_5\mathrm{Me_4}$); 158.96 ($\mathit{C}=\mathrm{CH_2}$); 160.93 ($C$(21)); 208.90 ($C$(22)). EI-MS (130 °C): *m*/*z* (relative abundance) 488 ($\mathrm{M}^{\bullet+}$; 7), 473 ($[\mathrm{M}-\mathrm{Me}]^+$; 5), 454 (12), 453 (32), 452 ($[\mathrm{M}-\mathrm{HCl}]^+$; 80), 451 (11), 450 (10), 355 (12), 354 (23), 353 (28), 352 ($[\mathrm{M}-\mathrm{L}]^+$; 29), 351 (13), 220 (49), 219 (37), 218 ($[\mathrm{M}-\mathrm{L}-\mathrm{C_5Me_4CH_2}]^+$; 100), 217 (45), 216 (37), 215 (22), 214 (15), 213 (40), 203 ($[\mathrm{M}-\mathrm{L}-\mathrm{Me}-\mathrm{C_5Me_4CH_2}]^+$; 11), 199 (12), 178 (10), 135 (51), 119 (42), 105 (21), 91 (22). IR (KBr, cm^{-1}): 3058 (w), 2990 (m), 2955 (vs), 2901 (s), 2865 (s), 2838 (m), 2718 (vw), 1600 (w), 1589 (vw), 1531 (m), 1493 (m), 1452 (s), 1440 (s), 1376 (vs), 1311 (vw), 1253 (vw), 1081 (vw), 1064 (vw), 1021 (m), 877 (m), 745 (w), 715 (w), 672 (vw), 597 (w), 507 (w), 448 (w), 415 (m). UV−vis (hexane, nm): 452 > 540 (sh). Anal. Calcd for $\mathrm{C_{30}H_{45}ClTi}$ (489.00): C, 73.68; H, 9.28. Found: C, 73.65; H, 9.25.

Preparation of 4g. Crystalline **3g** (0.35 g, 0.68 mmol) reacted with $\mathrm{PbCl_2}$ (0.11 g, 0.40 mmol) to give a red microcrystalline solid. Yield: 0.24 g (64%).

Data for **4g** are as follows. Mp: 162 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): 0.29 (s, 9H, $\mathrm{C(=CH_2)Si}\mathit{Me}_3$); 0.37 (s, 9H, $\mathrm{C(22)Si}\mathit{Me}_3$); 1.60, 1.92, 1.93, 2.56 (4 × s, 4 × 3H, $\mathrm{C_5}\mathit{Me}_4$); 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 3.07, 3.22 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 17.4 Hz, 2 × 1H, $\mathrm{C(6)}\mathit{H}_2$); 5.39, 5.75 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 2.4 Hz, 2 × 1H, $=\mathrm{C}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): 0.80, 8.17 ($\mathrm{Si}\mathit{Me}_3$); 10.88, 12.06 ($\mathrm{C_5}\mathit{Me}_4$); 12.86 ($\mathrm{C_5}\mathit{Me}_5$); 14.18, 15.84 ($\mathrm{C_5}\mathit{Me}_4$); 40.93 ($C$(6)); 117.09, 123.52, 126.45, 131.30, 134.07 ($\mathit{C}_5\mathrm{Me_4}$); 124.14 ($\mathit{C}_5\mathrm{Me_5}$); 127.08 ($=\mathit{C}\mathrm{H_2}$); 157.11 ($\mathit{C}=\mathrm{CH_2}$); 166.03 ($C$(21)); 215.54 ($C$(22)). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): − 14.13, − 5.80 ($\mathit{Si}\mathrm{Me_3}$). EI-MS (170 °C): *m*/*z* (relative abundance) (548, $\mathrm{M}^{\bullet+}$ not observed), 354 (54), 353 (24), 352 ($[\mathrm{M}-\mathrm{L}]^+$; 65), 317 ($[\mathrm{M}-\mathrm{L}-\mathrm{Cl}]^+$; 30), 220 (46), 219 (27), 218 ($[\mathrm{M}-\mathrm{L}-\mathrm{C_5Me_4CH_2}]^+$; 100), 217 (28), 216 (27), 215 (13), 213 (26), 181 (21), 119 (35), 73 (74). IR (KBr, cm^{-1}): 3058 (w), 2980 (sh), 2955 (s), 2898 (vs), 2718 (vw), 1484 (m), 1444 (m), 1407 (m), 1375 (s), 1298 (vw), 1245 (vs), 1168 (vw), 1064 (vw), 1018 (m), 941 (m), 928 (w), 897 (s), 845 (vs, b), 787 (w), 756 (s), 689 (m), 672 (m), 646 (w), 623 (w), 595 (vw), 574 (vw), 534 (vw), 482 (vw), 455 (w), 424 (m), 409 (s). UV−vis (hexane, nm): 435 > 545 (sh). Anal. Calcd for $\mathrm{C_{30}H_{49}ClSi_2Ti}$ (549.20): C, 65.61; H, 8.99. Found: C, 65.58; H, 9.02.

Preparation of 4h. Crude compound **3h** (0.52 g, 1.20 mmol) reacted with $\mathrm{PbCl_2}$ (0.18 g, 0.64 mmol) in THF to give a red solution. After evaporation of THF the residue was extracted with hexane. Cooling of the concentrated solution afforded a red waxy solid. This was, after drying under vacuum, used for its characterization.

Data for **4h** are as follows. ^{1}H NMR ($\mathrm{C_6D_6}$): 1.53 (s, 3H, $\mathrm{C(21)}\mathit{Me}$); 1.63 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 1.76, 1.78, 1.81, 2.53 (4 × s, 4 × 3H, $\mathrm{C_5}\mathit{Me}_4$); 2.92, 3.00 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 17.4 Hz, 2 × 1H, $\mathrm{C(6)}\mathit{H}_2$); 6.96−7.03 (m, 1H, *Ph*); 7.17−7.26 (m, 4H, *Ph*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): 11.31, 12.07 ($\mathrm{C_5}\mathit{Me}_4$); 12.66 ($\mathrm{C_5}\mathit{Me}_5$); 12.97, 14.33 ($\mathrm{C_5}\mathit{Me}_4$); 19.44 ($\mathrm{C(21)}\mathit{Me}$); 37.88 ($C$(6)); 118.92, 119.72 ($\mathit{C}_5\mathrm{Me_4}$); 123.82 ($\mathit{C}$H, *Ph*); 124.85 ($\mathit{C}_5\mathrm{Me_5}$); 126.73 ($\mathit{C}$H, *Ph*); 126.87, 129.67 ($\mathit{C}_5\mathrm{Me_4}$); 130.00 ($\mathit{C}$H, *Ph*); 141.38 ($\mathit{C}_5\mathrm{Me_4}$); 152.28 ($C_{ipso}$, *Ph*); 157.32 ($C$(21)); 207.17 ($C$(22)). EI-MS (170 °C): *m*/*z* (relative abundance) 468 ($\mathrm{M}^{\bullet+}$; 2), 455 (6), 453 ($[\mathrm{M}-\mathrm{Me}]^+$; 10), 354 (14), 353 (7), 352 ($[\mathrm{M}-\mathrm{L}]^+$; 20), 317 ($[\mathrm{M}-\mathrm{L}-\mathrm{Cl}]^+$; 38), 220 (44), 219 (25), 218 ($[\mathrm{M}-\mathrm{L}-\mathrm{C_5Me_4CH_2}]^+$; 100), 217 (27), 216 (25), 215 (12), 213 (24), 179 (21), 135 (12), 119 (14), 105 (11), 91 (8). IR (KBr, cm^{-1}): 3072 (vw), 3053 (w), 2989 (m), 2950 (m), 2901 (vs), 2853 (s, sh), 2720 (vw), 1589 (w), 1550 (vw), 1489 (m), 1435 (s), 1376 (vs), 1154 (vw), 1070 (w), 1019 (s), 916 (w), 790 (m), 769 (w), 756 (m), 742 (w), 708 (s), 701 (s), 620 (vw), 572 (vw), 513 (w), 467 (w), 415 (s). UV−vis (hexane, nm): 453 > 535 (sh). Anal. Calcd for $\mathrm{C_{29}H_{37}ClTi}$ (468.91): C, 74.28; H, 7.95. Found: C, 74.32; H, 8.00.

Preparation of 4i. The crude yellow oily **3i** (0.48 g, 1.20 mmol) reacted with $\mathrm{PbCl_2}$ (0.17 g, 0.62 mmol). Crystallization from hexane yielded a fine, crystalline red solid. Yield: 0.59 g (87%).

Data for **4i** are as follows. Mp: 200 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): 0.95 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 3H, $\mathrm{C(22)CH_2}\mathit{Me}$); 0.99 (t, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 3H, $\mathrm{C(21)CH_2}\mathit{Me}$); 1.60 (s, 3H, $\mathrm{C_5}\mathit{Me}_4$); 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 1.87−2.08 (m, partially overlapped 2H, $\mathrm{C(21)C}\mathit{H}_2$); 1.89, 1.94 (2 × s, 2 × 3H, $\mathrm{C_5}\mathit{Me}_4$); 2.15−2.30 (m, 1H, $\mathrm{C(22)C}\mathit{H}_2$); 2.41−2.58 (m, 1H, $\mathrm{C(22)C}\mathit{H}_2$); 2.43 (s, 3H, $\mathrm{C_5}\mathit{Me}_4$); 2.76, 2.84 (2 × d, 2 × $^2J_{\mathrm{HH}}$ = 16.8 Hz, 2 × 1H, $\mathrm{C(6)}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): 11.05, 12.10 ($\mathrm{C_5}\mathit{Me}_4$); 12.36 ($\mathrm{C(22)CH_2}\mathit{Me}$); 12.81 ($\mathrm{C_5}\mathit{Me}_5$); 13.74 ($\mathrm{C(21)CH_2}\mathit{Me}$); 14.00, 15.04 ($\mathrm{C_5}\mathit{Me}_4$); 24.02 ($\mathrm{C(21)}\mathit{C}\mathrm{H_2}$); 32.45 ($C$(6)); 33.30 ($\mathrm{C(22)}\mathit{C}\mathrm{H_2}$); 114.64, 123.02, 132.34, 133.61, the fifth signal is overlapped by solvent signal ($\mathit{C}_5\mathrm{Me_4}$); 123.68 ($\mathit{C}_5\mathrm{Me_5}$); 149.25 ($C$(21)); 212.45 ($C$(22)). EI-MS (190 °C): *m*/*z* (relative abundance) 436 (10), 435 (9), 434 ($\mathrm{M}^{\bullet+}$; 22), 421 (11), 420 (10), 419 ($[\mathrm{M}-\mathrm{Me}]^+$; 26), 399 (13), 398 ($[\mathrm{M}-\mathrm{HCl}]^+$; 36), 383 ($[\mathrm{M}-\mathrm{HCl}-\mathrm{Me}]^+$; 15), 352 ($[\mathrm{M}-\mathrm{L}]^+$; 5), 299 (11), 298 (9), 297 (25), 295 (17), 284 (11), 283 (16), 269 (12), 220 (42), 219 (42), 218 ($[\mathrm{M}-\mathrm{L}-\mathrm{C_5Me_4CH_2}]^+$; 100), 217 (67), 216 (37), 215 (30), 214 (17), 213 (52), 201 (10), 199 (14), 181 (11), 178 (12), 177 (10), 135 (12), 119 (31), 105 (16), 91 (20), 77 (11). IR (KBr, cm^{-1}): 2960 (s), 2903 (vs), 2866 (s), 2849 (sh), 2821 (m), 2720 (vw), 1565 (w), 1502 (m), 1490 (m), 1434 (s), 1377 (vs), 1308 (w), 1296 (vw), 1263 (w), 1192 (vw), 1146 (vw), 1079 (vw), 1057 (w), 1020 (m), 956 (vw), 818 (vw), 778 (vw), 754 (vw), 614 (vw), 598 (vw), 468 (w), 448 (m), 411 (s). UV−vis (hexane, nm): 430 > 515. Anal. Calcd for $\mathrm{C_{26}H_{39}ClTi}$ (434.89): C, 71.80; H, 9.04. Found: C, 71.82; H, 9.05.

Preparation of 4j. Crystalline **3j** (0.25 g, 0.67 mmol) reacted with $\mathrm{PbCl_2}$ (0.10 g, 0.35 mmol). After the usual workup procedure red polycrystalline material was obtained. Yield: 0.21 g (78%).

Data for **4j** are as follows. Mp: 95 °C. ^{1}H NMR ($\mathrm{C_6D_6}$, 323 K): 1.59 (s, 3H, $\mathrm{C(21)}\mathit{Me}$); 1.62 (s, 3H, $\mathrm{C_5}\mathit{Me}_4$); 1.80 (s, 3H, $\mathrm{C(22)}\mathit{Me}$); 1.83 (s, 15H, $\mathrm{C_5}\mathit{Me}_5$); 1.88, 1.94, 2.34 (3 × s, 3 × 3H, $\mathrm{C_5}\mathit{Me}_4$); 2.75 (br s, 2H, $\mathrm{C(6)}\mathit{H}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 323 K): 10.88, 12.08 ($\mathrm{C_5}\mathit{Me}_4$); 12.71 ($\mathrm{C_5}\mathit{Me}_5$); 13.85, 14.09 ($\mathrm{C_5}\mathit{Me}_4$); 16.77 ($\mathrm{C(21)}\mathit{Me}$); 29.57 ($\mathrm{C(22)}\mathit{Me}$); 36.43 ($C$(6)); 114.28, 122.71 ($\mathit{C}_5\mathrm{Me_4}$); 123.64 ($\mathit{C}_5\mathrm{Me_5}$); 132.92, 134.74, the fifths is overlapped by solvent signal ($\mathit{C}_5\mathrm{Me_4}$); 143.48 ($C$(21)); 206.98 ($C$(22)). EI MS (100 °C): *m*/*z* (relative abundance, %) 408 (13), 407 (15), 406 ($\mathrm{M}^{\bullet+}$; 21), 393 (9), 392 (8), 391 ($[\mathrm{M}-\mathrm{Me}]^+$; 20), 370 ($[\mathrm{M}-\mathrm{HCl}]^+$; 11), 356 (8), 355 ($[\mathrm{M}-\mathrm{Me}-\mathrm{HCl}]^+$; 23), 354 (11), 353 (20), 272 ($[\mathrm{M}-\mathrm{C_5Me_4CH_2}]^+$; 10), 269 (10), 257 (12), 256 (12), 255 ($[\mathrm{M}-\mathrm{HC_5Me_5}-\mathrm{HCl}]^+$; 29), 254 (7), 253 (12), 220 (38), 219 (33), 218 ($[\mathrm{M}-\mathrm{L}-\mathrm{C_5Me_4CH_2}]^+$; 100), 217 (45), 216 (257), 215 (17), 214 (9), 213 (27), 135 ($[\mathrm{C_5Me_5}]^+$; 16), 119 (16), 105 (12), 91 (13). IR (KBr, cm^{-1}): 2986 (m), 2949 (m, sh), 2902 (vs), 2836 (s), 2718 (vw), 1580 (w), 1498 (m), 1486 (m), 1442 (s), 1434 (s), 1375 (vs), 1298 (vw), 1190 (vw), 1064 (vw), 1048 (vw), 1021 (m), 956 (vw), 897 (vw), 829 (vw), 812 (vw), 789 (vw), 772 (vw), 689 (vw), 597 (vw), 499 (vw), 452 (m), 417 (s). UV−vis (hexane, nm): 440 (sh) > 515. Anal. Calcd for $\mathrm{C_{24}H_{35}ClTi}$ (406.84): C, 70.85; H, 8.67. Found: C, 70.86; H, 8.64.

Preparation of 4k. Crystalline **3k** (0.37 g, 0.65 mmol) reacted with $PbCl_2$ (0.10 g, 0.36 mmol). After the usual workup procedure yellowish brown crystalline material was obtained. Yield: 0.39 g (90%).

Data for **4k** are as follows. Mp: 218 °C. ^{1}H NMR (C_6D_6): 0.16 (s, 9H, C(21)Si*Me*$_3$); 0.38 (s, 3H, Si*Me*$_2$); 0.39 (s, 9H, C(24)Si*Me*$_3$); 0.51 (s, 3H, Si*Me*$_2$); 1.43, 1.74 (2 × s, 2 × 3H, C$_5$*Me*$_4$); 1.82 (s, 15H, C$_5$*Me*$_5$); 2.12, 2.18 (2 × s, 2 × 3H, C$_5$*Me*$_4$); 2.86, 2.94 (2 × d, 2 × $^2J_{HH} = 19.5$ Hz, 2 × 1H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): −0.88 (C(21)Si*Me*$_3$); 0.59, 3.43 (Si*Me*$_2$); 3.48 (C(24)Si*Me*$_3$); 10.11, 12.66 (C$_5$*Me*$_4$); 13.18 (C$_5$*Me*$_5$); 14.64, 14.75 (C$_5$*Me*$_4$); 31.04 (*C*H$_2$); 116.31, 117.95, 121.39 (*C*$_5$Me$_4$); 124.04 (*C*$_5$Me$_5$); 128.78 (*C*$_5$Me$_4$); 133.04 (*C*(21)); 137.03 (*C*$_5$Me$_4$); 165.84 (*C*(22)); 167.90 (*C*(24); 264.56 (*C*(23)). ^{29}Si{^{1}H} NMR (C_6D_6): −14.82 (*Si*Me$_3$); −5.65 (*Si*Me$_2$); 4.82 (*Si*Me$_3$). EI-MS (210 °C): *m/z* (relative abundance, %) 608 (12), 607 (25), 606 (51), 605 (50), 604 ($M^{\bullet+}$; 84), 603 (13), 602 (10), 569 ([M − Cl]$^+$; 5), 531 ([M − SiMe$_3$]$^+$; 5), 469 ([M − C$_5$Me$_5$]$^+$; 5), 396 ([M − C$_5$Me$_5$ − SiMe$_3$]$^+$; 7), 352 ([M − L]$^+$; 5), 317 ([M − L − Cl]$^+$; 13), 252 ([L]$^+$; 6), 237 ([L − Me]$^+$; 7), 220 (37), 219 (28), 218 ([M − L − C$_5$Me$_4$CH$_2$]$^+$; 100), 217 (33), 216 (24), 215 (10), 213 (16), 155 (11), 119 (10), 73 (81). IR (KBr, cm^{-1}): 2987 (sh), 2950 (s), 2899 (s), 2792 (w), 2720 (vw), 1562 (w), 1493 (m), 1435 (m), 1402 (w), 1388 (w), 1358 (s), 1246 (s), 1021 (w), 978 (s), 922 (m), 880 (s), 856 (vs), 835 (vs), 768 (s), 747 (m), 690 (m), 674 (w), 662 (w), 634 (m), 467 (m), 421 (m). UV−vis (hexane, nm): 490 (sh) > 600 (sh). Anal. Calcd for $C_{32}H_{53}Si_3ClTi$ (605.34): C, 63.49; H, 8.82. Found: C, 63.46; H, 8.80.

Preparation of 4l. Crystalline **3l** (0.32 g, 0.61 mmol) reacted with $PbCl_2$ (0.09 g, 0.33 mmol) in THF to give bright red crystals from hexane. Yield: 0.32 g (92%).

Data for **4l** are as follows. Mp: 205 °C. ^{1}H NMR (C_6D_6): 0.43, 0.48 (2 × s, 2 × 3H, Si*Me*$_2$); 1.14 (s, 9H, C(21)C*Me*$_3$); 1.26 (s, 9H, C(24)C*Me*$_3$); 1.44, 1.69 (2 × s, 2 × 3H, C$_5$*Me*$_4$); 1.86 (s, 15H, C$_5$*Me*$_5$); 2.23, 2.26 (2 × s, 2 × 3H, C$_5$*Me*$_4$); 2.77, 2.90 (2 × d, 2 × $^2J_{HH} = 19.5$ Hz, 2 × 1H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 0.85, 5.17 (Si*Me*$_2$); 10.71 (C$_5$*Me*$_4$); 13.36 (C$_5$*Me*$_5$); 13.49, 14.38, 15.46 (C$_5$*Me*$_4$); 28.49 (*C*H$_2$); 30.43 (C(21)C*Me*$_3$); 32.61 (C(24)C*Me*$_3$); 35.45 (C(24)*C*Me$_3$); 37.88 (C(21)*C*Me$_3$); 117.00, 117.47, 121.96 (*C*$_5$Me$_4$); 124.73 (*C*$_5$Me$_5$); 131.59 (*C*$_5$Me$_4$); 137.08, 137.21 (*C*(21) and *C*$_5$Me$_4$); 149.09 (*C*(22)); 170.42 (*C*24)); 240.69 (*C*(23)). ^{29}Si{^{1}H} NMR (C_6D_6): −6.89 (*Si*Me$_2$). EI-MS (200 °C): *m/z* (relative abundance, %) 574 (7), 573 (7), 572 ($M^{\bullet+}$; 13), 439 (6), 437 ([M − C$_5$Me$_5$]$^+$; 11), 221 (8), 220 (41), 219 (27), 218 ([M − L − C$_5$Me$_4$CH$_2$]$^+$; 100), 217 (24), 216 (18), 213 (9), 73 (15). IR (KBr, cm^{-1}): 2989 (m), 2945 (vs), 2899 (vs), 2858 (s), 2718 (vw), 1592 (vw), 1558 (vw), 1493 (m), 1481 (w), 1461 (m), 1437 (m), 1406 (w), 1387 (w), 1375 (s), 1359 (m), 1238 (s), 1204 (w), 1086 (w), 1055 (vs), 1020 (m), 919 (vw), 838 (vs), 819 (w), 778 (w), 764 (s), 696 (m), 673 (w), 615 (vw), 581 (vw), 499 (vw), 421 (m). UV−vis (hexane, nm): 470 (sh) ≫ 660. Anal. Calcd for $C_{34}H_{53}ClSiTi$ (573.19): C, 71.24; H, 9.32. Found: C, 71.19; H, 9.28.

Preparation of 4m. Crystalline **3m** (0.40 g, 1.16 mmol) reacted with $PbCl_2$ (0.18 g, 0.64 mmol) in THF (20 mL) to give a brown-yellow solution. Cooling of the concentrated solution afforded brown crystals. Yield: 0.40 g (91%).

Data for **4m** are as follows. Mp: 215 °C. ^{1}H NMR (C_6D_6): −0.42 (ddd, $J_{HH} = 5.4$ Hz, $J_{HH} = 11.1$ Hz, $J_{HH} =12.6$ Hz, 1H, TiC*H*$_2$); 1.39, 1.44, 1.68, 2.52 (4 × s, 4 × 3H, C$_5$*Me*$_4$); 1.78 (s, 15H, C$_5$*Me*$_5$); 1.88−1.96 (m, 1H, TiC*H*$_2$); 2.34−2.58 (m, 2H, TiCH$_2$C*H*$_2$); 2.66−2.83 (m, 2H, C$_5$*Me*$_4$C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 10.44, 11.29, 11.91 (C$_5$*Me*$_4$); 12.22 (C$_5$*Me*$_5$); 14.77 (C$_5$*Me*$_4$); 25.64 (C$_5$Me$_4$*C*H$_2$); 44.67 (TiCH$_2$*C*H$_2$); 80.58 (Ti*C*H$_2$); 115.18, 116.57, 117.97, 133.07, 143.09 (*C*$_5$Me$_4$); 122.20 (*C*$_5$Me$_5$). EI-MS (210 °C): *m/z* (relative abundance) 382 (9), 381 (8), 380 ($M^{\bullet+}$; 20), 365 ([M − Me]$^+$; 6), 354 (11), 353 (9), 352 (M − L]$^+$; 24), 345 (12), 344 ([M − HCl]$^+$; 33), 246 ([M − C$_5$Me$_4$CH$_2$]$^+$; 13), 221 (9), 220 (47), 219 (30), 218 ([M − L − C$_5$Me$_4$CH$_2$]$^+$; 100), 217 (25), 216 (25), 215 (8), 214 (6), 213 (13), 203 (9), 199 (8), 135 (13), 119 (15), 91 (11). IR (KBr, cm^{-1}): 3053 (vvw), 2980 (m), 2910 (vs, b), 2853 (s), 2829 (s), 2720 (vw), 1493 (m), 1435 (m), 1377 (s), 1312 (vw), 1301 (w), 1234 (vw), 1199 (w), 1163 (vw), 1117 (vw), 1060 (w), 1022 (m), 953 (vw), 926 (vw), 906 (vw), 871 (vw), 810 (vw), 680 (vw), 616 (w), 561 (vw), 549 (vw), 478 (w), 415 (s). UV−vis (hexane, nm): 395 (sh) > 475 (sh). Anal. Calcd for $C_{22}H_{33}ClTi$ (380.82): C, 69.38; H, 8.73. Found: C, 69.39; H, 8.78.

X-ray Crystallography. Single crystals or crystal fragments of **3a−g,k,l** and **4b,e,g,l,m** were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen. Diffraction data for all complexes except **3a** were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) and processed by the HKL program package.[27] Data for **3a** were collected on a CCD Xcalibur S (Mo Kα radiation, $\lambda = 0.710\,73$ Å) using φ-scan rotation. The phase problem was solved by direct methods (SIR97),[28] followed by consecutive Fourier syntheses, and refined by full-matrix least squares on F^2 (SHELXL-97).[29] Relevant crystallographic data are given in Table 5. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions and refined isotropically using the riding model, except for the hydrogen atoms on the methylene C(6) atom in **3b,e** and **4b,e,g,l**, the C(16) and C(26) atoms in two independent molecules of **3k**, the exo methylene C(27) atom in **3g**, and the C(24) atom in **4g**. These were found on difference Fourier maps and refined isotropically without any restraints.

Computational Details. DFT calculations have been performed at the Computer Center of the J. Heyrovsky Institute of Physical Chemistry of Academy of Sciences of the Czech Republic, v.v.i., using Gaussian 03, Revision C.02.[31] The transition state of **3j** was determined using the 6-31+G(d) basis set on all atoms and the BPW91 functional.[32] The Hessian needed for the geometry optimization was computed analytically. Vibration analysis for the transition-state molecule was done at the stationary point reached by the optimization procedure after checking for the presence of one (and only one) imaginary vibration. Vibrations and molecular orbitals were visualized by Molden.[33]

Acknowledgment. This research was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. IAA400400708) and the Ministry of Education, Youth and Sports (Project No. LC06070).

Supporting Information Available: CIF files for the structures of **3a−g,k,l** and **4b,e,g,l,m** and text giving the experimental procedure for obtaining **1**, a table giving the makeup of compounds **3a−m** and their UV−vis and ESR spectra, a table giving UV−vis spectral data for **4a−m**, figures giving 1D NOESY NMR spectra for **4a,b,c′,d,4g−j,m**, text giving the full ref 31, tables giving crystal data and Platon drawings at 30% probability for structures **3a−g,k,l** and **4b,e,g,l,m**, and a figure giving the optimized geometry of molecule **2a** with important interatomic distances. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800691F

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