Reviews

The Titanocene Complex of Bis(trimethylsilyl)acetylene: Synthesis, Structure, and Chemistry†

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In the context of the historical background in organosilicon chemistry of 1-silacyclopropenes the complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) was prepared by reduction of Cp_2TiCl_2 with magnesium in the presence of $Me_3SiC{\equiv}CSiMe_3$ in THF and characterized on the basis of structural and spectroscopic data as a 1-titanacyclopropene. Similar titanium and zirconium complexes, $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, Zr), as well as the corresponding zirconium complexes, $Cp'_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, with additional ligands L such as THF and pyridine were obtained later by the same procedure. Their reactivity toward unsaturated molecules in stoichiometric and catalytic reactions was investigated. By using different substituted Cp′ ligands, $Cp'_2 = Cp_2$, Cp^*_2, $(THI)_2$, EBTHI (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl, THI = tetrahydroindenyl, EBTHI = 1,2-ethylene-1,1′-bis(tetrahydroindenyl)), and additional ligands L (THF, pyridine) with these metals (Ti, Zr), a fine tuning of the reactions of these complexes was feasible. Additionally, the reactions are influenced by the steric properties of the substrate, the stoichiometry used, the solvents, and other reaction conditions. In the series of our investigations with these titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene it became well-established that the alkyne is an excellent spectator ligand which sufficiently stabilizes the metallocene fragment and which can be released quantitatively under mild conditions to generate the unstable and very reactive core complex. In this review we shall focus exclusively on special aspects of reactions of the titanocene complex of bis(trimethylsilyl)acetylene, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, as a typical titanacyclopropene. Returning to the aspects of organosilicon chemistry, it is shown that the isolobal 1-hetero-cyclopropenes, formed by the addition of the titanocene fragment Cp_2Ti: on one hand, and the dialkylsilylene R_2Si: on the other, to bis(trimethylsilyl)acetylene, are sometimes similar to each other in terms of their structures and reactivity.

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† In memory of Mark E. Vol'pin (May 23, 1923−Sept 28, 1996), and on the occasion of his 80th birthday.

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Introduction

The chemistry of titanocene complexes of bis(trimethylsilyl)acetylene has very strong roots in silicon chemistry, mostly that carried out by the group of Vol'pin in Moscow.[1a−c] In 1961 a contribution from this group predicted that silacyclopropenes should be a stable class of compounds on the basis of analogies to the cyclopropenyl cation.[1d,e] Later it became obvious that the compound obtained by the addition of dimethylsilylene to diphenylacetylene, PhC≡CPh, contained a six-membered ring: i.e., it was a dimer, rather than the claimed three-membered 1-silirene.[2] In 1976 true silirenes, three-membered-ring compounds containing a silicon atom and a C−C double bond, were reported for the first time.[3] Seyferth and co-workers using bis(trimethylsilyl)acetylene, $Me_3SiC{\equiv}CSiMe_3$, as the alkyne found that its reaction with hexamethylsilirane (a thermal dimethysilylene source) gave 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene as the first isolable 1-silacyclopropene.[3b]

Some years later Vol'pin and Shur in a reaction with diphenylacetylene, instead of a dialkylsilylene, used its isolobal analogue, titanocene (Cp_2Ti:), to prepare other unsaturated 1-heterocyclopropenes. After initially unsuccessful attempts,[4a] a titanacyclopropene, $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$, which contained no additional stabilizing ligand, was isolated in 1982 by one of the authors (V.V.B.) in an analytically pure state. However, crystals well-suited for a X-ray structure determination were not obtained.[4b,c] In 1985 Bercaw briefly mentioned the analogous permethyltitanocene complexes $Cp^*_2Ti(\eta^2\text{-}$

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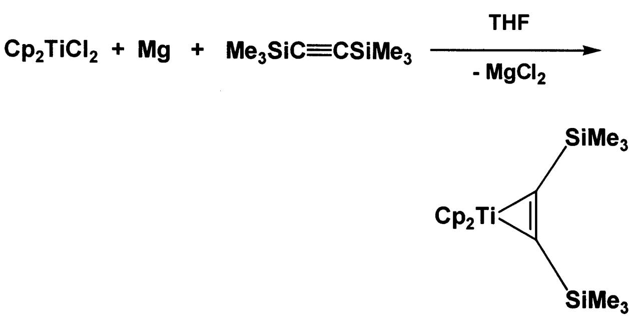
PhC_2Ph) and $Cp^*{}_2Ti(\eta^2\text{-}MeC_2Me)$, but also without X-ray crystal structures.[5]

After having investigated the influence of phosphorus ligands L and alkyne substituents R in nickel(0) complexes $L_2Ni(\eta^2\text{-}RC_2R)$,[6a] including a complex with bis(trimethylsilyl)acetylene, $(Ph_3P)_2Ni(\eta^2\text{-}Me_3SiC_2SiMe_3)$,[7] considered as 1-nickelacyclopropenes in Rostock, one of the authors (U.R.) joined the Vol'pin group in 1988 as a postdoctoral associate and became acquainted with titanocene chemistry. In cooperation with another author (V.V.B.) he continued more general investigations on the influence of early transition metals on alkyne complexation in the complexes $L_2M(\eta^2\text{-}RC_2R)$ (e.g., M = Ni, L = R_3P; M = Ti, Zr, L = Cp′, etc.).

With respect to the above-mentioned background from organosilicon chemistry, Vol'pin himself selected from all the suggested (by U.R.) alkynes bis(trimethylsilyl)acetylene as the most promising candidate for the project to prepare the stable titanocene−alkyne complex $Cp_2Ti(\eta^2\text{-}RC_2R)$ without additional ligands. Accordingly, the reduction of Cp_2TiCl_2 with magnesium in the presence of $Me_3SiC{\equiv}CSiMe_3$ in THF at room temperature (Scheme 1) was investigated. This reaction gave in high yield the stable, golden yellow complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**).[8a]

Scheme 1



(1)

Subsequently, this method was used for the synthesis of many other titanocene− and zirconocene−alkyne complexes (vide infra).

Structures

For a long time an X-ray crystal structure of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was not available. However, when the same method for preparation was followed, using

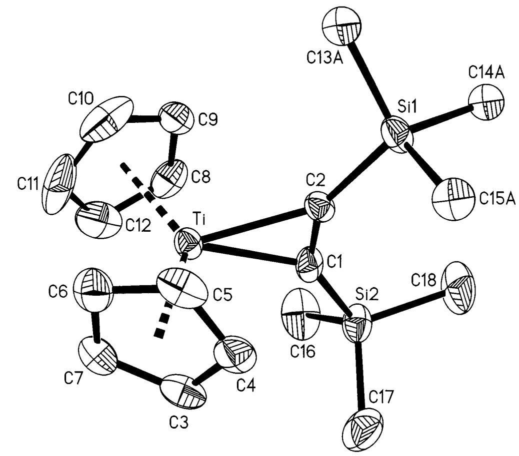


Figure 1. ORTEP plot of complex **1**. Hydrogen atoms and one position of the disordered group are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

variations of the Cp ligands and the alkyne substituents R, further work led to a number of titanium complexes of the type $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2R)$. These structures were determined by X-ray crystallography, e.g., first with Cp′ = Cp* and R = Me_3Si,[9] Ph,[9,10] and also with the unsubstituted Cp′ = Cp and R = Ph,[10] as well as that of the first alkyl-substituted example, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2{}^tBu)$.[11] Nevertheless, all attempts by different workers to obtain crystals of the parent compound $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ suitable for X-ray crystallography failed, due to its extremely high solubility in all inert solvents. Furthermore, during high-vacuum sublimation the complex slowly decomposed and did not give good crystals. Serendipitously, in an unanticipated way more than 12 years after its first synthesis, during unsuccessful reactions with substrates, suitable crystals of this titanocene complex were recoverd from the reaction mixtures (P.-M.P.).

The molecular structure of the compound (Figure 1) consists of a bent titanocene with the coordinated alkyne ligand located in the bisector plane (the angles between the TiC_2 unit and each Cp ligand plane are 21.5 and 25.2°, respectively).[8b]

The Cp ligand planes themselves form an angle of 46.6°. The carbon atoms of the alkyne and the Si atoms bonded to them form a nearly planar system with a torsion angle SiC_2Si of 6.5°. The coordinated triple bond of the alkyne (1.283(6) Å) in **1** is significantly longer compared to that of the free $Me_3SiC{\equiv}CSiMe_3$ molecule (1.208 Å) (see ref 12a and Table 1) and closer to the value of a typical double bond (1.331 Å)[13] (for the corresponding $Cp^*{}_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ the value is 1.308(3) Å). The distances between the titanium atom

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Table 1. Selected Metallocene Alkyne Complexes $Cp'_2Ti(\eta^2\text{-}RC_2R')$

	R = R′ = Me_3Si	R = Me_3Si; R′ = Ph	R = R′ = Ph
Alkynes RC≡CR′			
IR ν(C≡C) (cm^{-1})	2107	2160	2237
^{13}C NMR δ(C≡C) (ppm)	114.0	C−Si, 92.5; C−Ph, 104.4	90.1
X-ray d(C≡C) (Å)	1.208(3)[12a]	no data	1.210(3)[12b]
Complexes Cp'_2Ti			
$(\eta^5\text{-}C_5H_5)_2Ti$[8,10b,28]			
IR $\nu(C_2)$ (cm^{-1})	1687	1686	1713
^{13}C NMR $\delta(C_2)$ (ppm)	244.7	C−Si, 213.0; C−Ph, 219.6	196.5
X-ray $d(C_2)$ (Å)	1.283(6)	1.289(4)/1.279(4)	no data
$(\eta^5\text{-}C_5Me_5)_2Ti$[9,10b,28]			
IR $\nu(C_2)$ (cm^{-1})	1598, 1563	1625	1647
^{13}C NMR $\delta(C_2)$ (ppm)	248.5	C−Si, 213.2; C−Ph, 224.9	200.9
X-ray $d(C_2)$ (Å)	1.309(4)	1.308(3)	no data

Table 2. Selected Data for Titanocene and Zirconocene Complexes of Bis(trimethylsilyl)acetylene without/with Additional Stabilizing Ligands $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp'_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$

Cp'_2M or $Cp'_2M(L)$	IR $\nu(C_2)$ (cm^{-1})	NMR $\delta(C_2)$ (ppm)	X-ray $d(C_2)$ (Å)	ref
$(\eta^5\text{-}C_5H_5)_2Ti$	1687	244.7	1.283(6)	8, 10b, 28
$(\eta^5\text{-}C_5Me_5)_2Ti$	1598, 1563	248.5	1.309(4)	9, 10b, 28
$[\eta^5\text{-}C_5Me_4(p\text{-}F-C_6H_4)]_2Ti$	1598	251.6	1.303(3)	20a
$[\eta^5\text{-}C_5Me_4(SiMe_3)]_2Ti$	1595	246.4	1.313(4)	25a
$Me_2Si(\eta^5\text{-}C_5Me_4)_2Ti$	1608, 1578	254.9	1.297(5)	20b
$(\eta^5\text{-}C_5Me_4H)_2Ti$	1609	248.4	1.303(5)	28
$(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5(CH_2Ph)_5]Ti$	1601, 1589	244.8	1.300(7)	20c
$O[\eta^5\text{-}C_5Me_4(Me_2Si)]_2Ti$	1640, 1598	247.7	1.307(3)	20d
exo,exo-$[\eta^5\text{-}(SiMe_3)isodiCp]_2Ti$	1610	238.9	1.286(8)	20e
(*rac*-EBTHI)Zr	1534	259.7	1.300(10)	14
$(\eta^5\text{-}C_5Me_5)_2Zr$	1516	260.5	1.320(3)	17
$(\eta^5\text{-}C_5Me_4H)_2Zr$	1516	260.2	1.316(3)	17
$(\eta^5\text{-}C_5H_5)_2Zr(THF)$	1581	212.9	1.302(9)	15a
$(\eta^5\text{-}C_5H_5)_2Zr(pyridine)$	1579, 1599	220.5	1.312(3)	15b
$(\eta^5\text{-}C_5H_5)_2Zr$(*N*-Me-$\epsilon$-caprolactam)	1573	224.5	1.326(6)	51
$Me_2Si(\eta^5\text{-}C_5Me_4)_2Zr(pyridin)$	1597, 1579	218.5	1.297(6)	19a
(*rac*-EBTHI)Zr[(*S*)-(−)nicotine]	1560	no data	1.342(4)	19a
$(THI)_2Zr(THF)$	1559	222.0	1.340(7)	19b
$(THI)_2Zr(pyridine)$	1548, 1595	216.7	1.323(4)	19c

and the carbon atoms of the coordinated alkyne (2.136(5) and 2.139(4) Å) are in the range of endocyclic Ti−C(sp^2) σ-bonds (2.13−2.22 Å) (for the corresponding $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ the values are 2.122(3) and 2.126(3) Å). The CCSi angles of 145.7(4) and 147.8(4)° differ from 180° to approach a value of 120°, typical for sp^2-hybridized carbon atoms but not as great as that found in the Cp* case with 134.8(3) and 136.8(3)°. These data seem to prove that the structure of **1** is close to that of a titanacyclopropene.

Synthesis of Other Titanocene and Zirconocene Complexes with Bis(trimethylsilyl)acetylene

In the case of zirconium, following the same procedure under analogous conditions, at first only the corresponding complexes of the type $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with stabilizing ligands L = THF[15a] and pyridine[15b] were obtained. The complex with L = acetone existed only in an equilibrium with a zircon-adihydrofuran (Scheme 4).[15d]

The complex *rac*-(EBTHI)Zr(η^2-$Me_3SiC_2SiMe_3$) (Scheme 4), using Brintzinger's EBTHI ligand for conducting stereoselective reactions, was the first example of a fully characterized zirconocene−alkyne complex without an additional ligand.[14] Before that, only the complex $Cp^*_2Zr(\eta^2\text{-}PhC_2Ph)$ had been mentioned briefly,[16a] but it was not characterized in detail by spectroscopic and structural methods and was never published.[16b,c] Also, other compounds $Cp'_2Zr(\eta^2\text{-}Me_3SiC_2R)$ with, for example, Cp′ = Cp* and R = Me_3Si,[17] Ph[18] were prepared later.

In contrast to the titanocene chemistry described above it was shown by detailed dynamic NMR measurements that, depending on Cp′, some complexes, $Cp'_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, eliminate THF reversibly at higher temperatures to give the complexes $Cp'_2Zr(\eta^2$-

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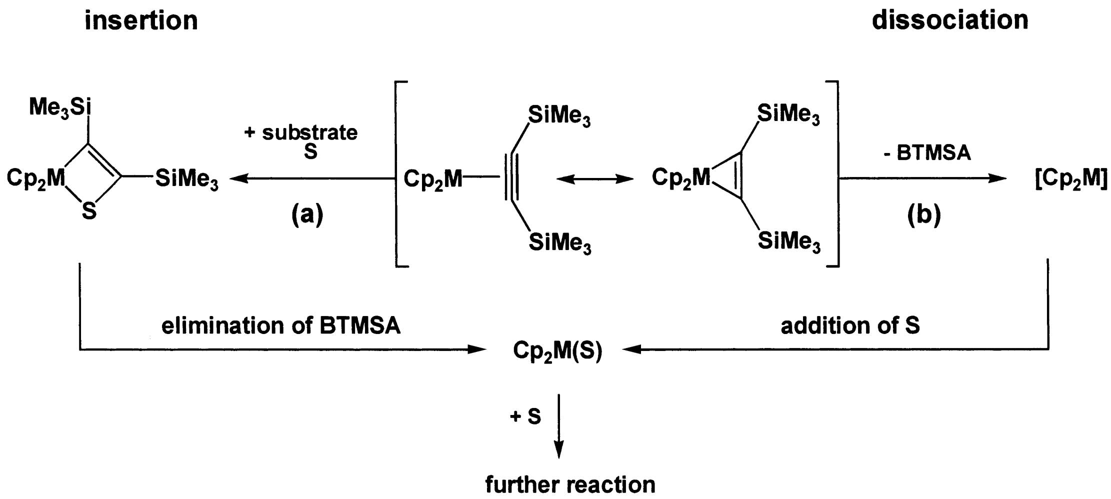
Scheme 2



$Me_3SiC_2SiMe_3$).[17,19b] The complex [$Cp_2Zr(\eta^2$-Me_3SiC_2-$SiMe_3$)] does not exist free in the absence of coordinated THF, but the complexes *rac*-(EBTHI)Zr(η^2-Me_3SiC_2-$SiMe_3$) and $Cp^*_2Zr(\eta^2$-$Me_3SiC_2SiMe_3$) did not coordinate with THF at any temperature investigated.[19a]

In many excellent contributions Mach and co-workers filled out the field of different substituted titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene by systematically conducted studies concerning the syntheses and chemistry of many other examples (see Table 2 and refs 17 and 20).

Today many examples of titanocene and zirconocene complexes of the type $Cp'_2M(\eta^2$-$Me_3SiC_2SiMe_3$) exist. Table 2 gives an overview of representative examples, which were characterized by X-ray crystal structure determinations. Also some ligand-stabilized complexes such as $Cp'_2Zr(L)(\eta^2$-$Me_3SiC_2SiMe_3$) are listed, but only monomeric complexes were considered. Special types of complexes, e.g., with bridging bis(trimethylsilyl)acetylene ligands, which are formed during syntheses when an excess of magnesium and of bis(trimethylsilyl)-acetylene was used (see Scheme 24),[21b,c] or ligands other than Cp′ ligands are not included here.[21]

The Metal−Alkyne Interaction

On the basis of the spectroscopic and structural data of the complexes (Tables 1 and 2), a description in terms of two resonance hybrids may be discussed: as acetylenic π-complexes (+2 oxidation state) or as metallacyclopropenes (+4 oxidation state) (Scheme 2; BTMSA = bis(trimethylsilyl)acetylene).

One can tune the metal−alkyne interaction by changing the metal (titanium or zirconium) or the cyclopentadienyl ligand Cp′ as well as the additional ligands L.

The observed trends (larger coordination shifts in the IR and ^{13}C NMR data as well as longer C−C bond distances) indicate a stronger complexation of the alkyne in complexes with zirconium and/or pentamethylcyclopentadienyl ligands (compared to titanium and cyclopentadienyl). If an additional ligand L is used, the interaction of the alkyne with the metal becomes weaker (Table 2).

The influence of the alkyne substituents on the coordination to the metal is more complex. For complexes with a late transition metal such as Ni(0) a correlation of the inductive parameters of the substituents R with the coordination shifts in the IR and ^{13}C NMR spectra was described:[6a,b] e.g., for Ph larger coordination shifts of the alkyne were found (compared to Me_3Si). A similar result was found in the IR data for the early transition metals titanium and zirconium, but in the ^{13}C NMR spectra the reverse case was established.[6c] Thus, in the ^{13}C NMR spectra of complexes with R = Me_3Si larger shifts were observed compared to those for R = Ph (Table 1). Unsymmetrically substituted complexes (Ph and Me_3Si) give upon coordination a smaller polarization of the carbon atoms for Ti (compared to the free alkyne). This also is the case for Ni(0) complexes.[6d] This was assumed to be a result of electron delocalization in the 1-titanacyclopropenes.[4b,6d]

In general, these interactions lead to two basic types of reactions of the metallacyclopropene: (a) insertion of the substrate into the metallacyclopropene ring and (b) dissociation of the alkyne with formation of a reactive metallocene fragment which subsequently is trapped by reaction with substrate.

General Considerations

The released group 4 metallocene fragments titanocene, "Cp_2Ti", and zirconocene, "Cp_2Zr", are un-

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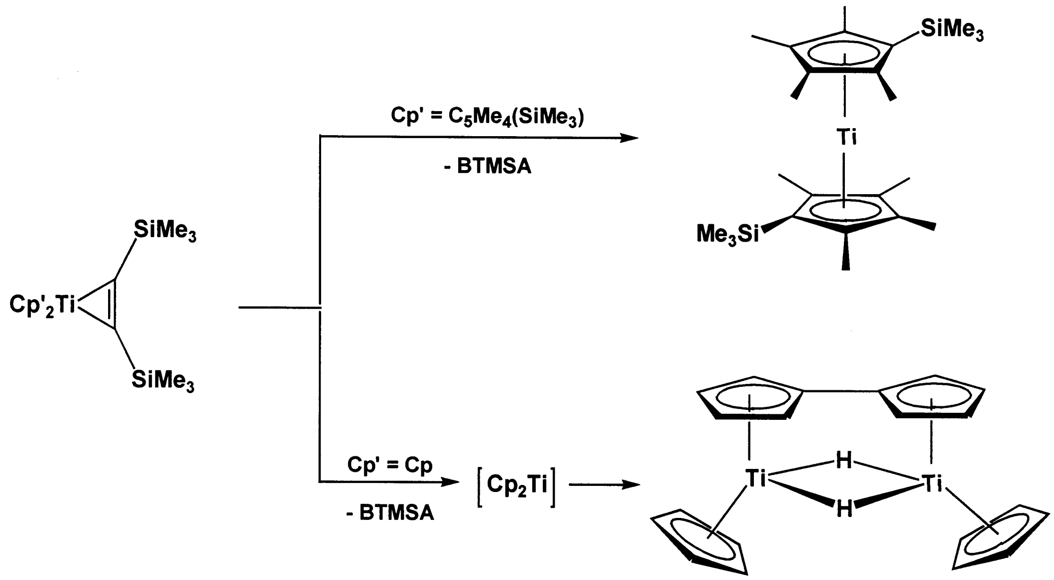
(20) (a) Kupfer, V.; Thewalt, U.; Tislerova, I.; Stepnicka, P.; Gyepes, R.; Kubista, J.; Horacek, M.; Mach, K. *J. Organomet. Chem.* **2001**, *620*, 39. (b) Varga, V.; Hiller, J.; Gyepes, R.; Polasek, M.; Sedmera, P.; Thewalt, U.; Mach, K. *J. Organomet. Chem.* **1997**, *538*, 63. (c) Schmid, G.; Thewalt, U.; Polasek, M.; Mach, K.; Sedmera, P. *J. Organomet. Chem.* **1994**, *482*, 231. (d) Horacek, M.; Stepnicka, P.; Kubista, J.; Gyepes, R.; Cisarova, I.; Petrusova, L.; Mach, K. *J. Organomet. Chem.* **2002**, *658*, 235. (e) Horacek, M.; Stepnicka, P.; Gentil, S.; Fejfarova, K.; Kubista, J.; Pirio, N.; Meunier, P.; Gallou, F.; Paquette, L. A.; Mach, K. *J. Organomet. Chem.* **2002**, *656*, 81. (f) Varga, V.; Mach, K.; Hiller, J.; Thewalt, U.; Sedmera, P.; Polasek, M. *Organometallics* **1995**, *14*, 1410.

(21) (a) Horacek, M.; Hiller, J.; Stepnicka, P.; Mach, K. *J. Organomet. Chem.* **1998**, *571*, 77. (b) Varga, V.; Mach, K.; Schmid, G.; Thewalt, U. *J. Organomet. Chem.* **1993**, *454*, C1. (c) Varga, V.; Mach, K.; Schmid, G.; Thewalt, U. *J. Organomet. Chem.* **1994**, *475*, 127. (d) Hiller, J.; Thewalt, U.; Podlaha, J.; Hanus, V.; Mach, K. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1551.

Scheme 3



stable 14-electron species in a d^2 configuration having the oxidation state M(II). Possessing one lone electron pair and two vacant valence orbitals, they can, in terms of their reactivity, be compared to carbenes. The interactions between occupied and unoccupied orbitals can explain why these metallocenes, "Cp_2M", react with a variety of unsaturated compounds to form metallacycles.

There are some established systems which generate titanocene or zirconocene very well: e.g., mixtures of Cp_2ZrCl_2 with ^nBuLi which form via $Cp_2Zr(\sigma\text{-}^nBu)_2$ the complex $Cp_2Zr(\pi$-1-butene) (Negishi) and of Cp_2ZrCl_2 with EtMgCl which form via $Cp_2Zr(\sigma\text{-Et})_2$ the complex $Cp_2Zr(\pi$-ethylene) (Takahashi), sometimes stabilized by additional ligands as in complexes such as $Cp_2Zr(R_3P)$-(π-1-butene) (Binger) and $Cp_2Ti(PMe_3)(\pi$-ethylene) (Alt). Also, complexes such as $Cp_2Ti(PMe_3)_2$ (Alt) and Cp_2Zr-(π-1,3-butadiene) (Erker) were frequently used. These and other examples are summarized in a number of excellent reviews and various informative contributions in textbooks.[22] The success of these systems in certain reactions often depends on their preparative accessibility, on the selectivity of the conversions, and on the inertness of the stand-in ligand. From this point of view, all the above-mentioned systems have certain disadvantages. Nevertheless, they are frequently and successfully used in organic synthesis, sometimes without any knowledge of the elemental organometallic reactions involved. To study these basic steps of stoichiometric and catalytic reactions, the complexes with bis(trimethylsilyl)acetylene are sometimes better suited.

Mechanistic Considerations

The special feature of bis(trimethylsilyl)acetylene in most reactions of its complexes is the ability to stabilize the metallocene core and the tendency to suppress coupling reactions of the alkyne, first described in 1988 by Fagan and Nugent[23] and in 1989 by Livinghouse.[24]

Two general possibilities for reactions exist: insertion of substrate into the metallacyclopropane ring (path a in Scheme 2) or extrusion and trapping of the Cp_2M^{II} species from the metallacyclopropene (path b). The predominant reaction behavior of complexes $Cp_2M(L)(\eta^2$-$Me_3SiC_2SiMe_3)$ for M = Ti without L or M = Zr with L = THF, pyridine, is best explained by the ready release of the alkyne. This formation of complexes "Cp_2M-(substrate)" can occur after dissociation of the alkyne (Scheme 2, right side: dissociation/addition) or after coupling of the coordinated alkyne with the substrate (Scheme 2, left side: insertion/elimination) from the formed metallacycle. For zirconium strong hints have been found for an additive mechanism, while for titanium the dissociation via a free titanocene is more likely. Such a dissociation in the case of the titanocene–alkyne complexes $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, $Cp' = \eta^5$-$C_5Me_4(SiMe_3)$, Cp, finds additional support in the investigations of Mach (Scheme 3),[25] who reported that the complex $[\eta^5\text{-}C_5Me_4(SiMe_3)]_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ gives, after dissociation of the alkyne, the *stable, free* titanocene $[\eta^5\text{-}C_5Me_4(SiMe_3)]_2Ti$ in the absence of any ligand (Scheme 3), a type of compound which was first

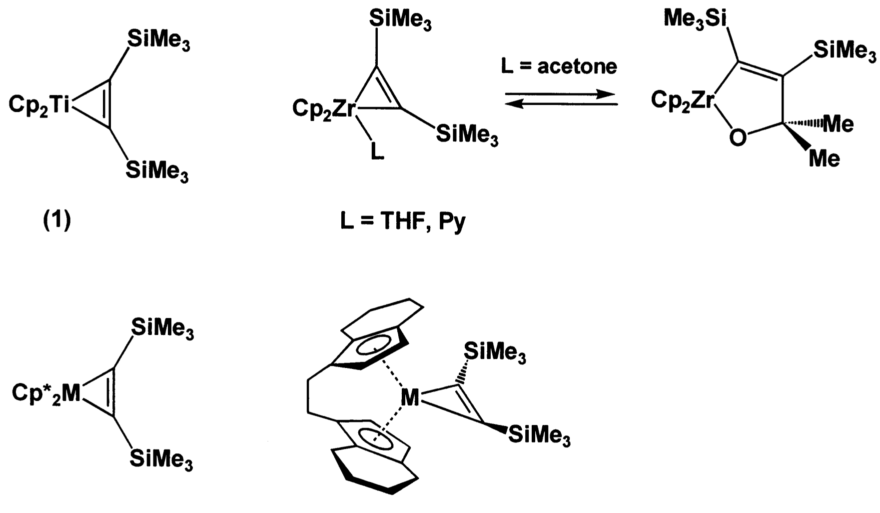
(22) (a) Negishi, E.; Takahashi, T. *Aldrichim. Acta* **1985**, *18*, 31. (b) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (c) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (e) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (f) Buchwald, S. L.; Fisher, R. A. *Chim. Scr.* **1989**, *29*, 417. (g) Negishi, E. *Chim. Scr.* **1989**, *29*, 457. (h) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. (i) Buchwald, S. L.; Broene, R. D. *Science* **1993**, 1696. (j) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (k) Hanzawa, Y.; Ito, H.; Taguchi, T. *Synlett* **1995**, 299. (l) Maier, E. L. *Nachr. Chem. Technol. Lab.* **1993**, *41*, 811. (m) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755. (n) Beckhaus, R. *Nachr. Chem. Technol. Lab.* **1998**, *46*, 611. (o) Negishi, E.; Montchamp, J.-L.: Zirconocenes. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 241. (p) Beckhaus, R.: Titanocenes. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 153. (q) Negishi, E.; Huo, S. Synthesis and Reactivity of Zirconocene Derivatives. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 1. (r) Takahashi, T.; Li, Y. Zirconacyclopentadienes in Organic Synthesis. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 50.

(23) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(24) Van Wagenen, B. C.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495.

(25) (a) Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, *18*, 3572. (b) Lukesova, L.; Horacek, M.; Stepnicka, P.; Fejfarova, K.; Gyepes, R.; Cisarova, I.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2002**, *663*, 134.

Scheme 4



M = Ti, Zr   M = Ti, Zr

reported by Lawless.[26] It is impossible to prepare this free titanocene directly starting from $[\eta^5\text{-}C_5Me_4(SiMe_3)]_2$-$TiCl_2$ by reduction with magnesium, because coupling reactions of the substituted Cp′ ligands predominate.[27] This example once again nicely illustrates the advantage of using the bis(trimethylsilyl)acetylene complex route. The free titanocene $[\eta^5\text{-}C_5Me_4(SiMe_3)]_2Ti$ is able to coordinate ethylene, forming $[\eta^5\text{-}C_5Me_4(SiMe_3)]_2Ti$-$(\eta^2\text{-}C_2H_4)$.[25]

On the other hand, if no substrate was present, the thermolysis of the unsubstituted complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ gave in high yield (μ-η^5:η^5-fulvalene)bis(μ-hydrido)bis(η^5-cyclopentadienyl)titanium as a "dimeric titanocene" (Scheme 3), resulting from the well-known intermolecular stabilization of the free titanocene $[(\eta^5\text{-}C_5H_5)_2Ti]$ formed after dissociation of the alkyne.[28] If there are any substrates present in solution, they coordinate to the free titanocene, forming the basis for the chemistry described below.

Stoichiometric Reactions

In a series of investigations with titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene it was well established that the alkyne is an excellent spectator ligand which sufficiently stabilizes the metallocene fragment and which can be released quantitatively under mild conditions to generate the unstable and highly reactive core complex. By using different substituted Cp′ ligands (Cp, Cp*, EBTHI), additional ligands L (THF, pyridine), and the metals (Ti, Zr) a fine tuning of the reactions of these complexes was feasible.

(26) Hitchcock, P. B.; Kerton, F. M.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 10264.
(27) Horacek, M.; Hiller, J.; Polasek, M.; Mach, K. *Organometallics* **1997**, *16*, 4185.
(28) Varga, V.; Mach, K.; Polasek, M.; Sedmera, P.; Hiller, J.; Thewalt, U.; Troyanov, S. I. *J. Organomet. Chem.* **1996**, *506*, 241.
(29) (a) Ohff, A.; Pulst, S.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (b) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (c) Rosenthal, U.; Burlakov, V. V. Organometallic Chemistry of Titanocene and Zirconocene Complexes with Bis(trimethylsilyl)acetylene as the Basis for Applications in Organic Synthesis. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 355. (d) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *J. Organomet. Chem.*, in press.

Additionally, the reactions are influenced by the steric properties of the substrate, the stoichiometry used, the solvents, and other reaction conditions.

The complexes of various titanocenes and zirconocenes obtained by their reactions with bis(trimethylsilyl)-acetylene can be used for the synthesis of different organic and element-organic compounds. Representative examples for the investigated complexes are shown in Scheme 4.

An overview of their chemistry is given in Scheme 5, whereas more general aspects,[29a] their reactivity toward di- and polyynes,[29b] and examples of their potential for organic syntheses,[29c] as well as their role in C−C single-bond cleavage and coupling reactions,[29d] have been summarized earlier. Similar results were described recently.[22r]

In this review we shall focus exclusively on special aspects of reactions of the titanocene complex Cp_2Ti-$(\eta^2\text{-}Me_3SiC_2SiMe_3)$ as a typical titanacyclopropene. Interesting comparisons to the Cp* and/or Zr variations have been published earlier and are not considered here.[18b,29]

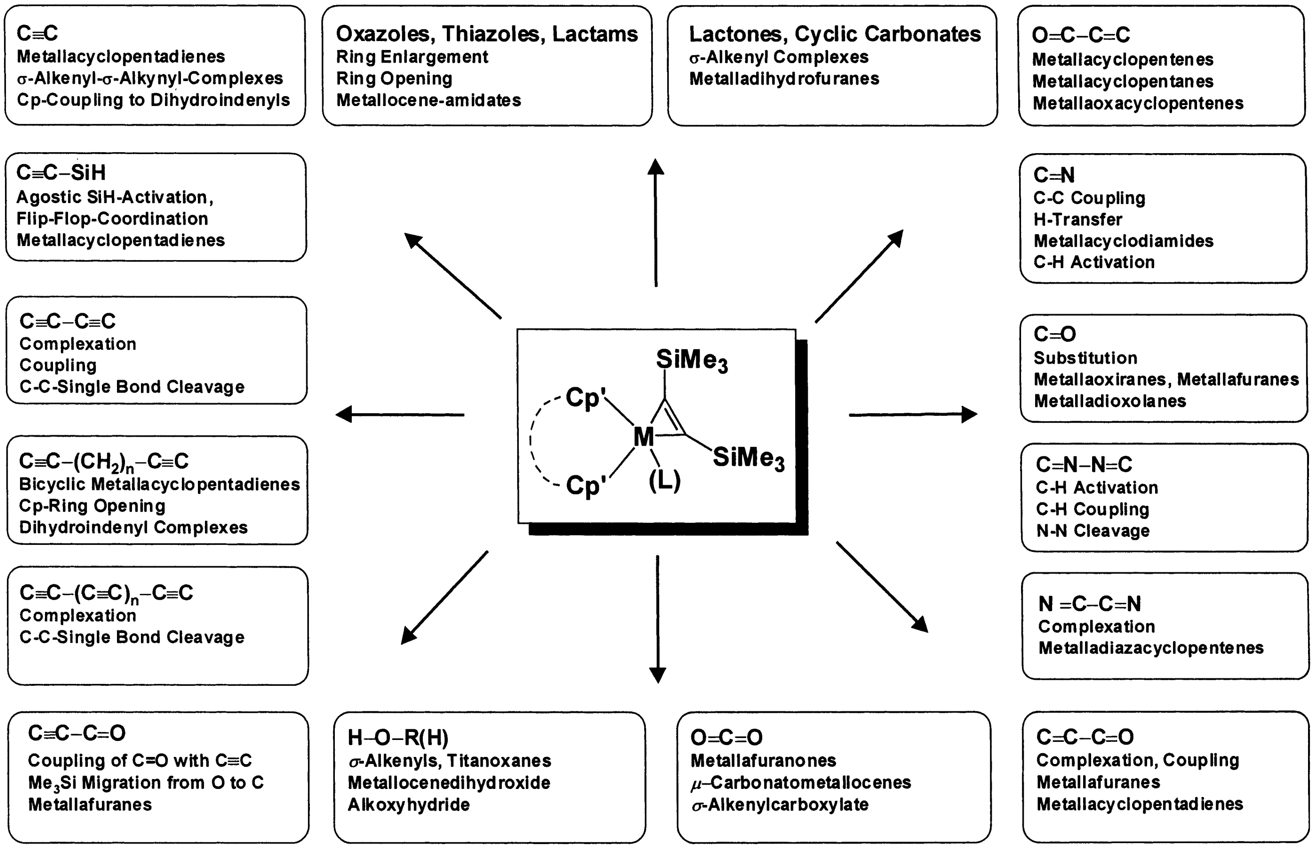
Alkynes Including Acetylene. Bis(trimethylsilyl)-acetylene alone does not react with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**), but in the presence of magnesium a reaction takes place (see below and Scheme 24).

Tolane, PhC≡CPh, reacts with **1** by substitution of the bis(trimethylsilyl)acetylene. When this reaction was carried out using an excess of **1**, the main product was the tolane complex of titanocene, $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$. With additional tolane, the tetraphenyl-substituted titanacylopentadiene $Cp_2Ti(C_4Ph_4)$ was produced (Scheme 6).[8a,10b,22r]

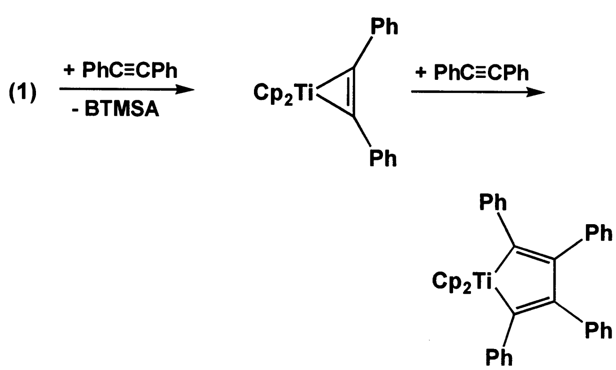
This was the first example which established the substitution of the bis(trimethylsilyl)acetylene by a substrate. Later also bis(trimethylstannyl)acetylene, $Me_3SnC{\equiv}CSnMe_3$, was shown to react with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) to give by substitution of the alkyne the complex $Cp_2Ti(\eta^2\text{-}Me_3SnC_2SnMe_3)$.[20f]

With the unsymmetrically substituted $Me_3SiC{\equiv}CPh$ the kinetically favored, unsymmetrically substituted titanacyclopentadiene was formed first which, after

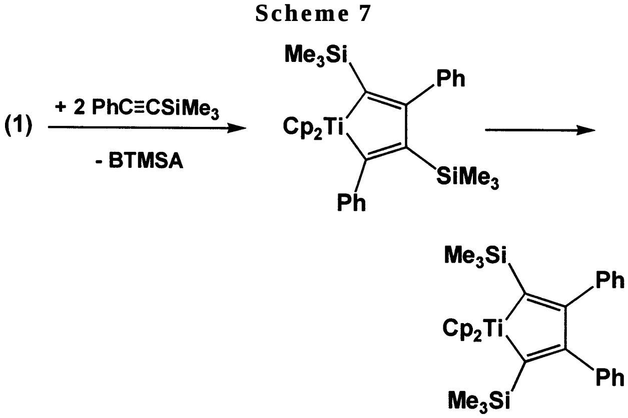
Scheme 5



Scheme 6



Scheme 7



cycloreversion, gave the symmetrically substituted and thermodynamically more stable isomer (Scheme 7).[11]

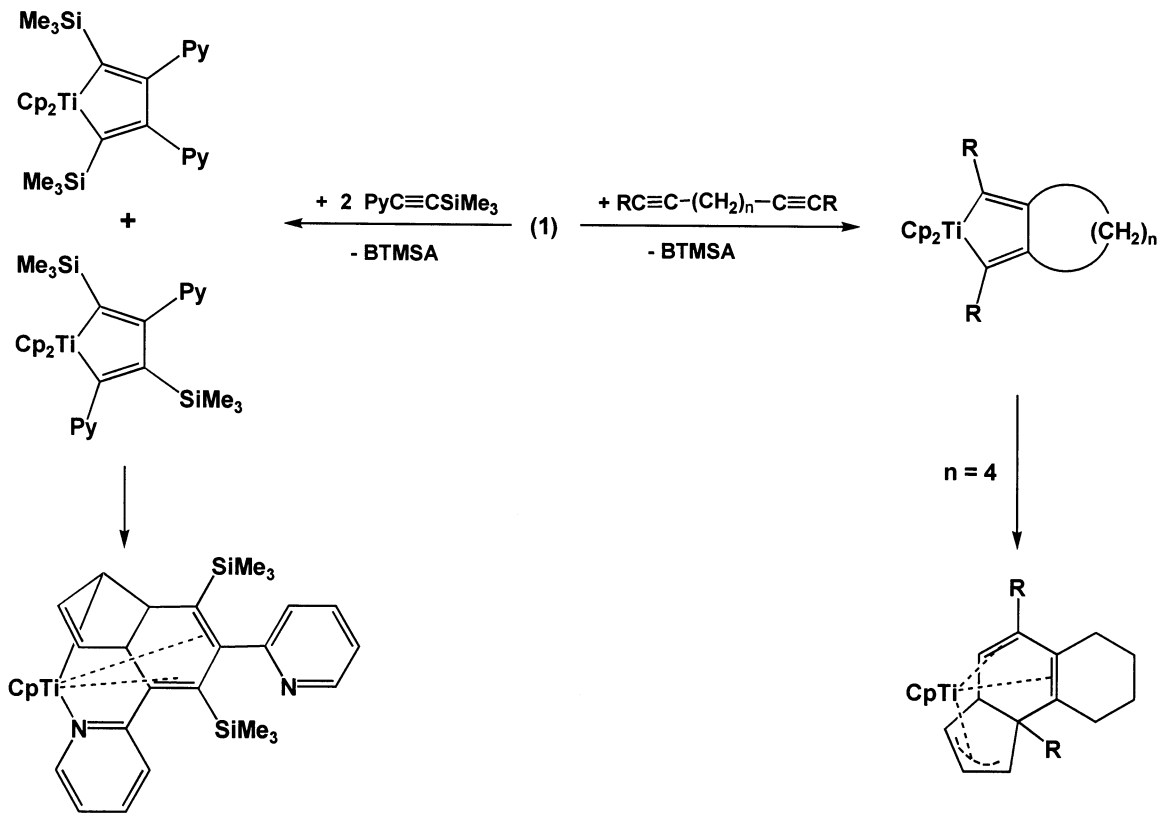
Due to steric reasons, the other symmetrical product with both Me_3Si groups in the 3,4-positions was not formed. This regioselectivity is typical also for other unsymmetrically substituted alkynes, $Me_3SiC{\equiv}CR$. For instance, the corresponding pyridyl-substituted acetylene $Me_3SiC{\equiv}CPy$ yielded with **1**, in the manner described above, first the kinetically favored unsymmetrically substituted complex in addition to the symmetrically substituted thermodynamically more stable product. Here also the symmetrical 3,4-$(Me_3Si)_2$ product was not formed. It is remarkable that on standing in solution the unsymmetrically substituted complex gave an unusual coupling of one Cp ligand with the tetrasubstituted metallacyclopentadiene unit with formation of a dihydroindenyl complex (Scheme 8).[30]

Reactions of complex **1** with different α,ω-diynes, $RC{\equiv}C(CH_2)_nC{\equiv}CR$, gave, after displacement of the bis(trimethylsilyl)acetylene and via intramolecular cyclization, bicyclic titanacyclopentadienes. The stability of the products is determined by the spacer length. For $n = 2$, 4 the compounds were isolated but decomposed for $n = 5$ to undefined compounds. For $n = 4$ the product rearranged slowly, by C–C cleavage of the Cp ligand and intramolecular coupling (Scheme 8), to a stable tricyclic η^4:η^3-dihydroindenyl titanium complex[31] which is similar to the above-mentioned product of $Me_3SiC{\equiv}CPy$ and also to the compound formed as the final product in the reaction of **1** with acetylene, described below (Scheme 9).

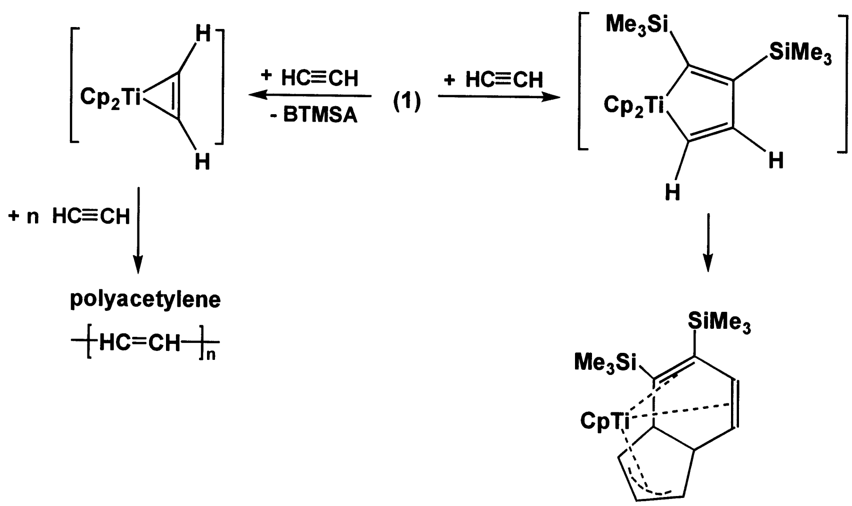
Detailed in situ NMR investigations showed that in the reaction of **1** with acetylene at low temperature a

(30) Rosenthal, U.; Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *J. Organomet. Chem.* **1995**, *503*, 221.
(31) Tillack, A.; Baumann, W.; Ohff, A.; Lefeber, C.; Spannenberg, A.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 187.

Scheme 8



Scheme 9



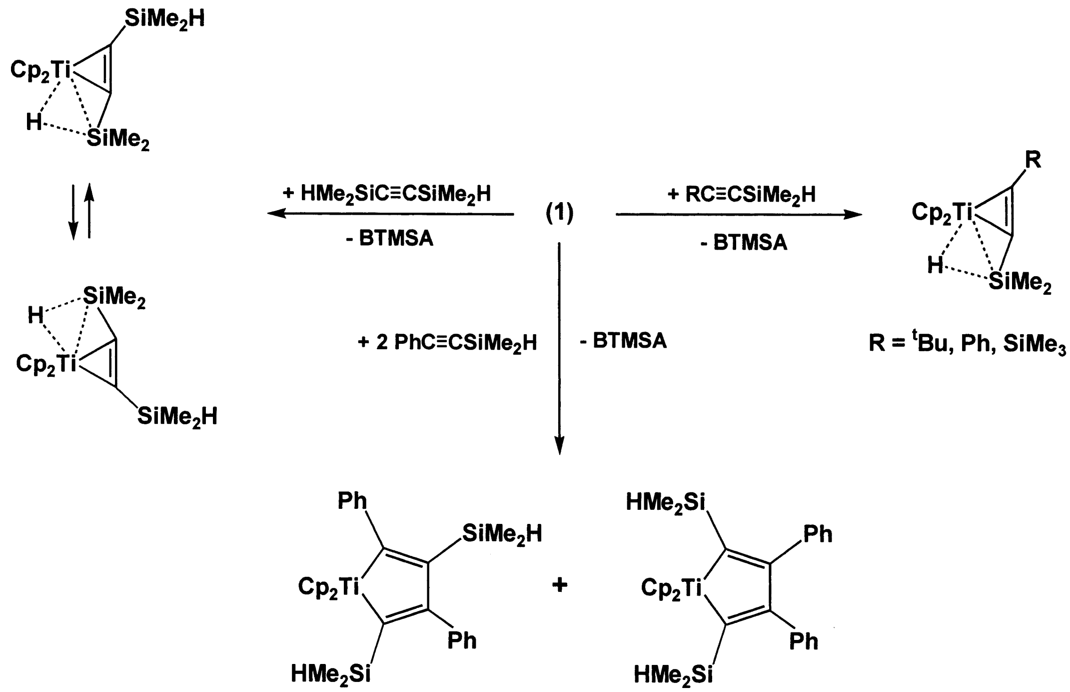
disubstituted titanacyclopentadiene was formed by insertion (Scheme 9) in addition to the *trans*-polyacetylene (see below).[32] Warming these reaction mixtures gave a dihydroindenyl complex as the result of an unusual coupling of one intact Cp ligand with the diene unit. This is important for deactivation processes of the catalyst in the polymerization of acetylene.[32] The unisolated product, $[Cp_2Ti(\eta^2\text{-}HC_2H)]$, formed by substitution of the bis(trimethylsilyl)acetylene from complex **1** acting as a precatalyst, seems to be the real catalyst for the polymerization of acetylene.

Alkynylhydrosilanes. The acetylene exchange in complex **1** with 1 equiv of an alkynylsilane, $RC\equiv CSiMe_2H$ (R = ^{t}Bu, Ph, $SiMe_3$, $SiMe_2H$), yielded complexes in which an agostic interaction between the Si−H bond with the metal center is realized, giving a trans configuration of the complexed alkyne (Scheme 10).[33] Using the more bulky Cp* ligand instead of Cp prevents such an interaction. The reaction of **1** with the difunctional substrate $HMe_2SiC\equiv CSiMe_2H$ resulted in a flip-flop coordination. These complexes with intramolecularly coordinating alkynylsilanes serve as suitable model compounds for the study of the intermolecular interaction of similar alkyne complexes with silanes, which are

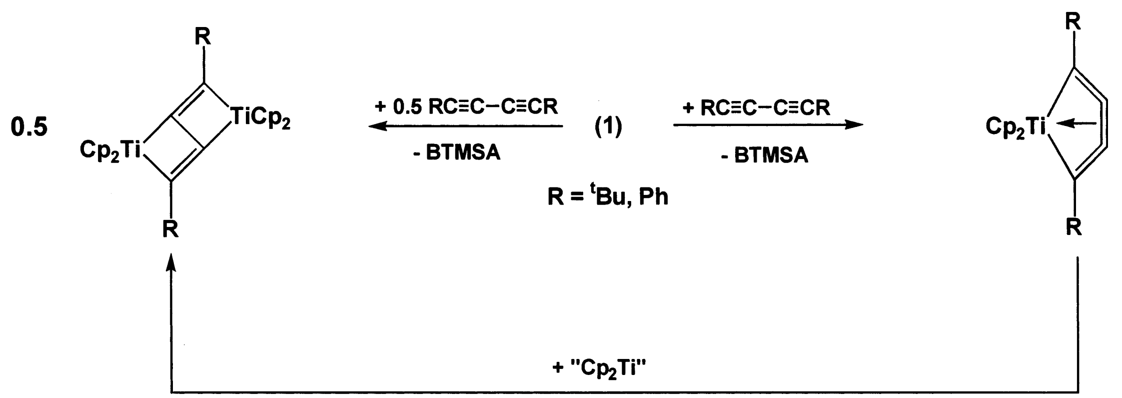
(32) Thomas, D.; Peulecke, N.; Burlakov, V. V.; Heller, B.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U.; Beckhaus, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 919.

(33) (a) Ohff, A.; Kosse, P.; Baumann, W.; Tillack, A.; Kempe, R.; Görls, H.; Burlakov, V. V.; Rosenthal, U. *J. Am. Chem. Soc.* **1995**, *117*, 10399. (b) Peulecke, N.; Ohff, A.; Kosse, P.; Tillack, A.; Kempe, R.; Spannenberg, A.; Baumann, W.; Burlakov, V. V.; Rosenthal, U. *Chem. Eur. J.* **1998**, *4*, 1852.

Scheme 10



Scheme 11



used in catalytic reactions such as the hydrosilylation of aldimines and ketimines and the dehydrogenative polymerization of silanes. They allow a study of the influence of different Cp ligands and metals on the catalytic activity of complexes.

With 2 mol of $PhC{\equiv}CSiMe_2H$ complex **1** produced the symmetrical titanacyclopentadiene with the two Ph groups at the 3,4-positions. In this complex an Si−H interaction with the titanium was not observed.

1,3-Butadiynes. All reactions of disubstituted 1,3-butadiynes with **1** strongly depend on the substituents and the stoichiometry. The products, generally obtained after elimination of the bis(trimethylsilyl)acetylene, cover a wide spectrum.[29a,b] Sometimes cleavage of the butadiynes, reverse coupling with formation of other butadiynes, and different coupling reactions of two butadiynes in the coordination sphere of one metal or between two metals were observed. The main products of these reactions were summarized in several reviews.[29a,b,34]

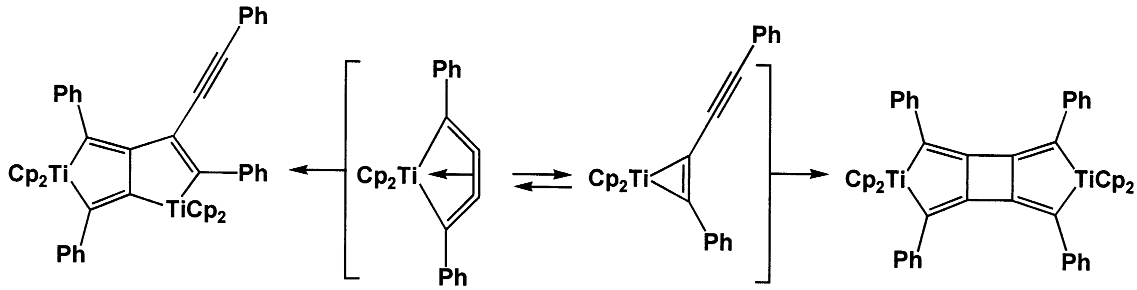
(a) Complexation. In the reactions of 2 equiv of complex **1** with butadiynes $RC{\equiv}CC{\equiv}CR$, e.g., R = Ph, ^{t}Bu, the type of well-known binuclear complexes with intact C_4 units between the two metal centers was found.[35] The former diynes were transformed to “zig-zag butadiene ligands” or μ-η(1−3):η(2−4)-*trans*,*trans*-tetradehydrobutadiene moieties between two metallocene cores (Scheme 11). Additionally, besides this 2:1 complexation of the titanocene, a 1:1 complexation was observed when employing a different stoichiometry. The butadiynes, $RC{\equiv}CC{\equiv}CR$, with R = ^{t}Bu, Ph generate the five-membered titanacyclocumulenes (metallacyclopenta-2,3,4-trienes, η^4-butadiyne complexes).[36]

(34) (a) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2002**, *48*, 71. (b) Lotz, S.; Van Rooyen, H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219. (c) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79. (d) Choukroun, R.; Cassoux, P. *Acc. Chem. Res.* **1999**, *32*, 494. (e) Lang, H.; Weinmann, M. *Synlett* **1996**, 1. (f) Lang, H.; Rheinwald, G. *J. Prakt. Chem.* **1999**, *341*, 1. (g) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206*–*207*, 102.

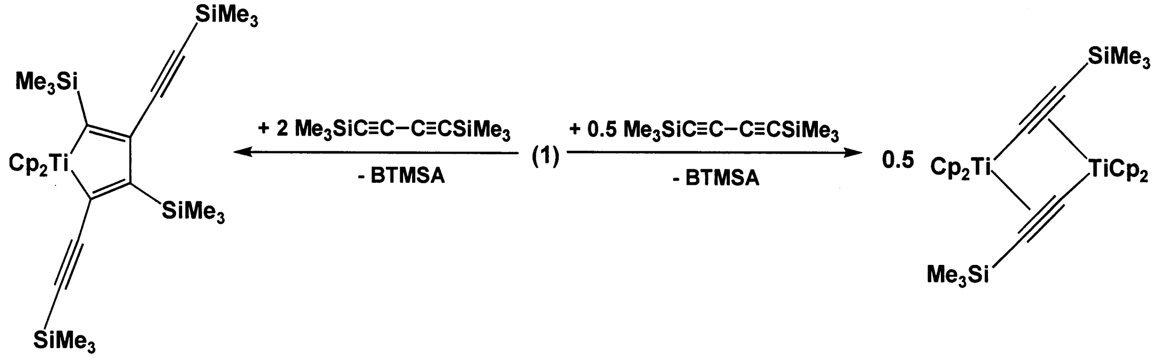
(35) (a) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W.; Görls, H. *J. Organomet. Chem.* **1994**, *468*, C4. (b) Rosenthal, U.; Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *Organometallics* **1994**, *14*, 2961.

(36) (a) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967. (b) Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *536*–*537*, 293.

Scheme 12



Scheme 13



Such five-membered metallacyclocumulenes are very unusual, but similar five-membered hetarynes had been suggested as reactive intermediates by Wittig in the early 1960s.[37] The structures of titanacyclocumulenes show an almost planar arrangement of the metallacycle, containing three C−C double bonds, of which the central one is elongated. This elongation is ascribed to the intramolecular interaction of this bond with the metal center, making this type of complex stable. The distances and the angles (70−74° at C-α and 147−150° at C-β) in the metallacycle are in good agreement with theoretical calculations, which additionally had shown that titana- and zirconacyclocumulenes are thermodynamically more stable than the isomeric bis(σ-acetylide) complexes.[38] All four carbon atoms of the former diyne are viewed as having p orbitals perpendicular to the plane of the cyclocumulene. The sp-hybridized internal C atoms possess additional p orbitals in that plane which are used to establish a coordination of that bond to the metal center.

Reactions of the titanacyclocumulenes suggest that an equilibrium occurs between a η^4 complex (titanacyclocumulene) and a η^2 complex (titanacyclopropene) (Scheme 12).[39a] This is supported by recent theoretical calculations[39b,c] and some reactions. One example is given in Scheme 12.

Evidently, the components of the equilibrium mixture react with each other to afford an unsymmetrical complex in which a titanacyclopentadiene is annelated to a titanacyclopentene.[39a] This can be rationalized in terms of an insertion of the internal double bond of the titanacyclocumulene into the titanacyclopropene. Additionally, the symmetrical titanium-substituted radialene is generated in the same solution. This can be thought of as a formal dimerization of two titanacyclocumulene molecules. Interaction of the titanacyclocumulenes with additional titanocene sources **1** can give alternatively complexes with intact diynes[35] or 2-fold σ,π-alkynyl-bridged metal(III) complexes[40] (cf. single-bond cleavage).

(b) Coupling Reactions of 1,3-Butadiynes. In the reaction of complex **1** with 2 equiv of the diyne $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ a regioselective coupling of the diynes to a titanacyclopentadiene was observed, which has one alkynyl group in an α-position and another in a β-position with regard to the metal (Scheme 13). [36a]

This product of the coupling of two diynes at a single titanium center is in contrast to the above-mentioned examples of coupling reactions of two diynes between two titanocene fragments.

(c) Single-Bond Cleavage in 1,3-Butadiynes. Changing only the stoichiometry of the conversion can alter the reaction pathway to cleavage reactions if 2 equiv of the metallocene reacts with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (Scheme 13).[40] The generated products are, from a formal point of view, 2-fold σ,π-alkynyl-bridged metal(III) complexes. There is a strong influence of the substituents R attached to the butadiynes, $RC{\equiv}CC{\equiv}CR$, as can be exemplified by the trimethylsilyl group, which profoundly activates the inner C−C single bond by its β effect.[41]

Linear Tetraynes RC≡CC≡CC≡CC≡CR. The reaction behavior of **1** toward linear octatetraynes, RC≡

(37) Wittig, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 415.

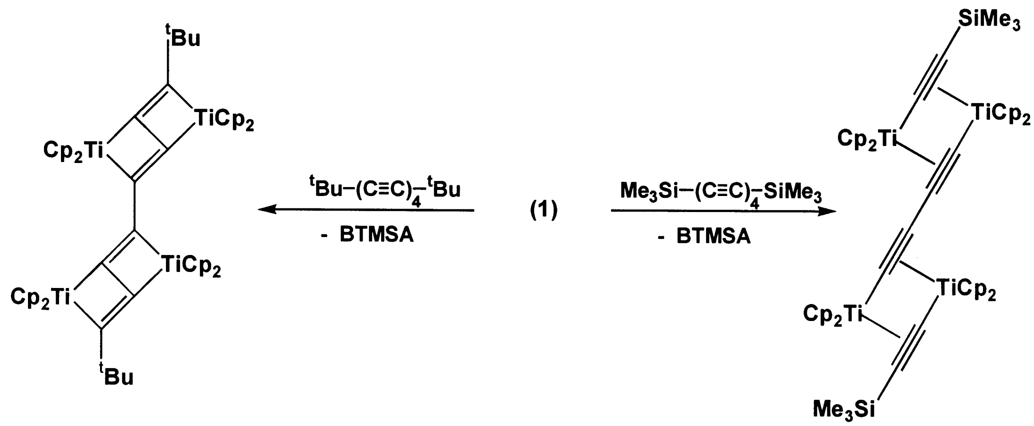
(38) (a) Pavankumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125. (b) Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952.

(39) (a) Pellny, P.-M.; Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Francke, V.; Rosenthal, U. *J. Organomet. Chem.* **1999**, *578*, 125. (b) Jemmis, E. D.; Phukan, A. K.; Rosenthal, U. *J. Organomet. Chem.* **2001**, *635*, 204. (c) Jemmis, E. D.; Phukan, A. K.; Giju, A. T. *Organometallics* **2002**, *21*, 2254.

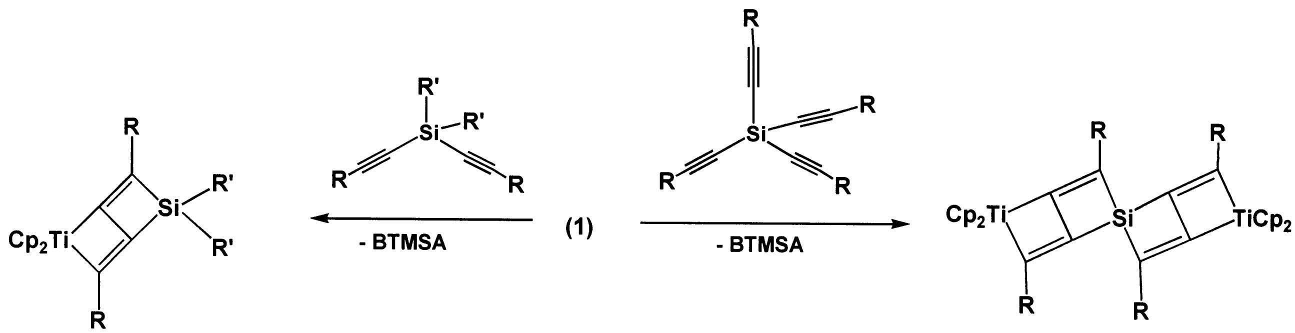
(40) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C 36.

(41) Jemmis, E. D.; Giju, K. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 606.

Scheme 14



Scheme 15



CC≡CC≡CC≡CR, is very similar to that found for the 1,3-butadiynes (Scheme 14).

Four equivalents of **1** on reaction with $^tBuC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C^tBu$ formed a complex with an intact C_8 chain between four titanocene centers, whereas with $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ a 2-fold C−C single-bond cleavage was observed.[42]

Branched Tetraynes $(RC{\equiv}C)_4Si$ and Diynes $(RC{\equiv}C)_2SiR'_2$. Reactions of the branched tetraalkynylsilanes $(RC{\equiv}C)_4Si$, R = ^tBu, Ph, Me_3Si, with **1** led, via 2-fold migration and C−C coupling of alkynyl groups, to a novel type of dinuclear carbon-rich spiro complexes (Scheme 15).[43a]

The conversions proved to be independent of the substituents and the stoichiometry employed. Also, the zirconocene sources, $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$, were used instead of complex **1**.[43a]

Reactions of the branched dialkynylsilanes $(RC{\equiv}C)_2SiR'_2$ (R = R′ = Ph; R = Ph, R′ = Me; R = ^tBu, R′ = Me) with **1** led, via similar migration and C−C coupling of an alkynyl group, to silacyclobutene-annelated titanacyclobutene complexes (Scheme 15).[43b] Such complexes with intact C_4 units as “zig-zag butadiene ligands” or μ-$\eta(1{-}3)$:$\eta(2{-}4)$-*trans,trans*-tetradehydrobutadiene between two different centers were described also for zirconium and silicon.[43c,d]

(42) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Tillack, A.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed.* **1997**, *36*, 2615.

(43) (a) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2000**, *19*, 1198. (b) Horacek, M.; Bazyakina, N.; Stepnicka, P.; Gyepes, R.; Cisarova, I.; Bredeua, S.; Meunier, P.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2001**, *628*, 30. (c) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665. (d) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842.

Branched Hexaynes 1,3,5-$(RC{\equiv}CC{\equiv}C)_3C_6H_3$. Tris(butadiynyl)benzenes such as 1,3,5-$(RC{\equiv}CC{\equiv}C)_3C_6H_3$ gave products in which no cleavage of the C−C single bonds had occurred when 6 equiv of **1** was used (Scheme 16).[44]

In general, the hexaynes and the tetraynes show a reaction pattern similar to that found for the 1,3-butadiynes.

Heteroolefins. In reactions of complex **1** with benzophenone, acetone, or formaldehyde no defined complexes could be isolated, but with benzaldehyde the titanadioxacyclopentane was produced via an elimination of bis(trimethylsilyl)acetylene (Scheme 17).[45]

In the reaction of **1** with the ketimine $PhN{=}CH_2$ a hydrogen transfer generated the complex $Cp_2Ti(-N{=}CPh_2)(-NHCHPh_2)$ (Scheme 17).[46]

1,4-Diazabutadienes, RN=CHCH=NR, reacted with complex **1** with liberation of the alkyne and formation of the corresponding diazadiene complexes. This represents a new, general method for the preparation of 1-metalla-2,5-diazacyclopent-3-ene derivatives of titanocenes in high yield (Scheme 18).[47]

In analogous reactions of differently substituted azines, RR′C=NN=CRR′ (Scheme 19), the products once again depended on the substituents R and R′. With R = R′ = Me substitution of the alkyne by the azine and subsequent CH activation were observed. In the case

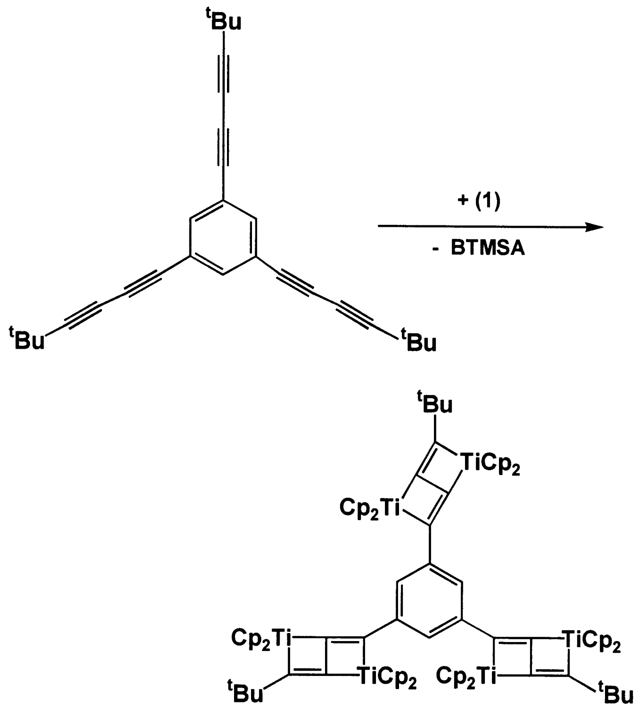
(44) Pellny, P.-M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1999**, *18*, 2906.

(45) Kempe, R.; Spannenberg, A.; Peulecke, N.; Rosenthal, U. *Z. Kristallogr.* **1998**, *213*, 425.

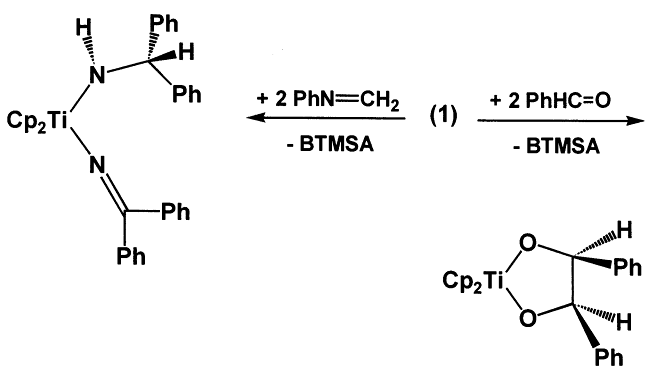
(46) Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1995**, *14*, 3090.

(47) (a) Ohff, A.; Zippel, T.; Arndt, P.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 1649. (b) Zippel, T.; Arndt, P.; Ohff, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429.

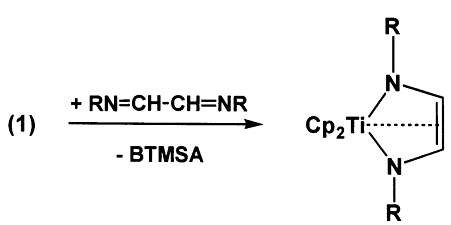
Scheme 16



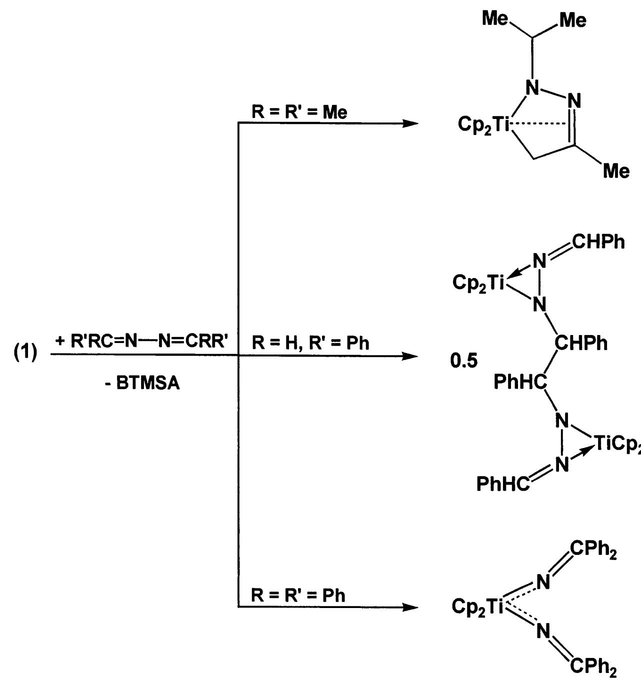
Scheme 17



Scheme 18



Scheme 19



of the azine where R = H and R′ = Ph, the acetylene was also displaced and, by reductive coupling of two azine molecules, a binuclear Ti(III) complex was formed. When R = R′ = Ph, the central N−N single bond of the azine was cleaved to form a bis(imido) complex.[47]

Ketoximes and aldoximes behaved differently (Scheme 20). Aliphatic and alicyclic O-silylated ketoximes, $R_2C{=}NOSiMe_3$, reacted with complex **1** with elimination of the alkyne and N−O bond cleavage to give imido−silanolates,[48] whereas the corresponding aldoxime, $PhCH{=}NOSiMe_3$, yielded the titanadiazacyclopentene in addition to unisolated titanocene nitrile complexes.[49]

The reactions of the titanocene source **1** with carbon dioxide gave, by elimination of 50% of the alkyne, a binuclear complex. A titanafuranone was formed by air oxidation of the latter (Scheme 21).[50a,b]

This isolated intermediate is of interest, because a complex of similar composition had been proposed in the reaction of CpCp*Ti(η^2-PhC_2Ph) with carbon dioxide. However, this compound was neither isolated nor characterized.[50c]

Heterocyclic Compounds. Lactams represent a special type of C=N system due to the tautomerization between the lactam (keto amine) and lactim (hydroxyimine) forms. The lactim form is much more favored in cyclic than in noncyclic carboxamides. The reaction of complex **1** with ϵ-caprolactam gave, after elimination of the alkyne and of molecular hydrogen, a complex with a deprotonated lactam in a η^2-amidate bonding fashion (Scheme 22).[51]

Complex **1** reacted with 2,2′-bipyridyl and 4,5-diazafluorene with displacement of the alkyne and electron transfer to the bipyridyl ligand to form a radical anion (Scheme 23).[52]

Reaction with Magnesium and Bis(trimethylsilyl)acetylene. If complex **1** was treated with magnesium and bis(trimethylsilyl)acetylene in THF, after a transfer of one Cp ligand from titanium to magnesium, a titanium−magnesium complex containing two perpendicularly bridging bis(trimethylsilyl)acetylene ligands,

(48) Tillack, A.; Arndt, P.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 737.

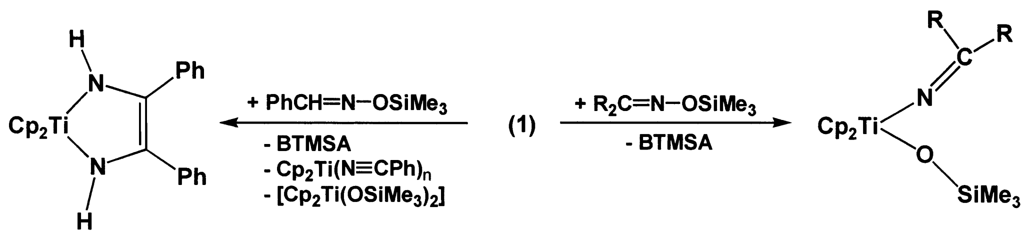
(49) Tillack, A.; Arndt, P.; Spannenberg, A.; Kempe, R.; Zippel, T.; Rosenthal, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 2038.

(50) (a) Burlakov, V. V.; Rosenthal, U.; Yanovsky, A. I.; Struchkov, Yu. T.; Ellert, O. G.; Shur, V. B.; Vol'pin, M. E. *Organomet. Chem. USSR* **1989**, *2*, 1193. (b) Burlakov, V. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Shur, V. B.; Ellert, O. G.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *542*, 105 and references therein. (c) Demerseman, B.; Mahe, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394.

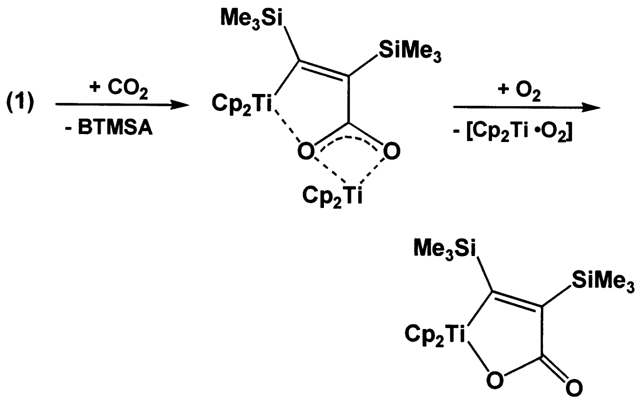
(51) Arndt, P.; Lefeber, C.; Tillack, A.; Rosenthal, U. *Chem. Ber.* **1996**, *129*, 1281.

(52) (a) Witte, P.; Klein, R.; Kooijman, H.; Spek, A. L.; Polasek, M.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1996**, *519*, 195. (b) Gyepes, R.; Horacek, M.; Cisarova, I.; Mach, K. *J. Organomet. Chem.* **1998**, *551*, 207.

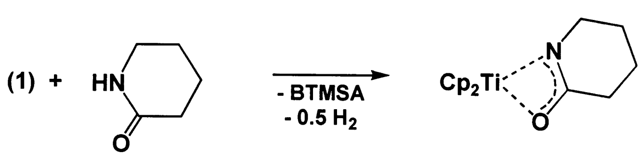
Scheme 20



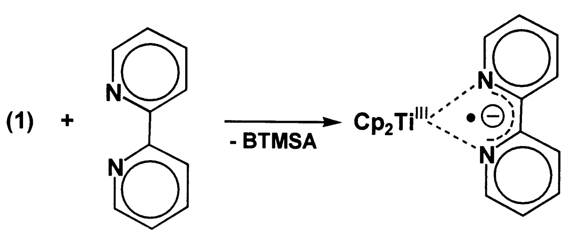
Scheme 21



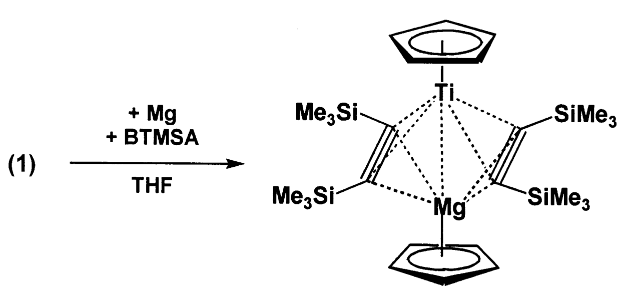
Scheme 22



Scheme 23



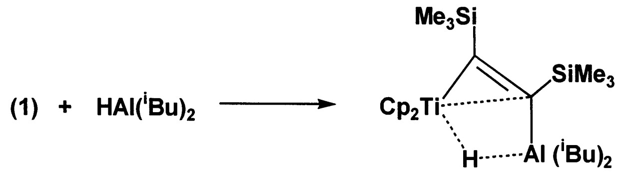
Scheme 24



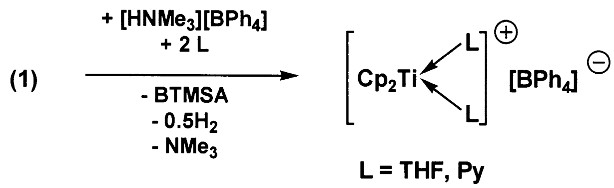
[CpTi](μ-η^2:η^2-$Me_3SiC_2SiMe_3$)$_2$[CpMg], was formed (Scheme 24).[21b,c]

Reactions with Lewis Acids. Complex **1** reacts smoothly with triisobutylaluminum with elimination of isobutene to give the bimetallic complex [Cp_2Ti](μ-η^1:η^2-$Me_3SiCCSiMe_3$)(μ-H)[Al(^{i}Bu)$_2$]. The latter could be prepared even better by direct addition of diisobutylaluminum hydride to the alkyne complex (Scheme 25).[53]

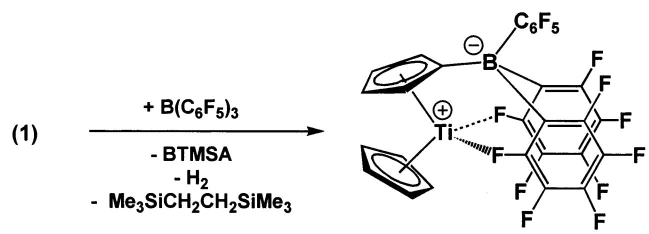
Scheme 25



Scheme 26



Scheme 27



In the reaction of **1** with the Brønsted acid [$HNMe_3$][BPh_4] cationic, paramagnetic d^1 titanocene(III) complexes [Cp_2TiL_2]$^+$[BPh_4]$^-$ with the ligand THF or pyridine were formed via a 1e oxidation of the 14e unit with evolution of molecular hydrogen and displacement of the alkyne (Scheme 26).[54]

The reaction of **1** with $B(C_6F_5)_3$ in toluene produced the zwitterionic titanium(III) complex CpTi[η^5-C_5H_4B-(C_6F_5)$_3$] by electrophilic substitution of a hydrogen atom of one of the η^5-C_5H_5 rings by the $B(C_6F_5)_3$ molecule (Scheme 27).[55] A characteristic feature of this zwitterionic complex is the presence of coordinative bonds between the ortho fluorine atoms of two C_6F_5 substituents and the positively charged titanium center. The air oxidation of this complex afforded the titanoxane {Cp[η^5-$C_5H_4B(C_6F_5)_3$]Ti}$_2$O, which contains two zwitterionic units in the molecule.[56] In each of these units,

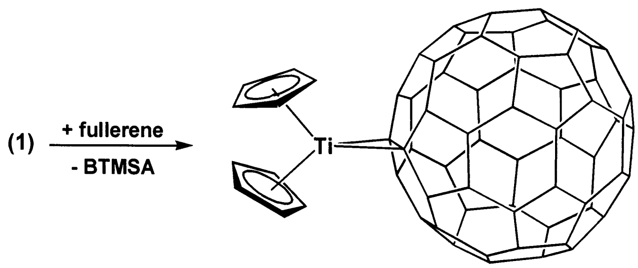
(53) Arndt, P.; Spannenberg, A.; Baumann, W.; Becke, S.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2001**, 2885.

(54) (a) Ohff, A.; Kempe, R.; Baumann, W.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 241. (b) Ohff, A.; Kempe, R.; Baumann, W.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *532*, 281.

(55) (a) Burlakov, V. V.;Troyanov, S. I.; Letov, A. V.; Mysov, E. I.; Furin, G. G.; Shur, V. B. *Izv. Akad. Nauk, Ser. Khim.* **1999**, 1022; *Russ. Chem. Bull. (Engl. Transl.)* **1999**, *48*, 1012. (b) Burlakov, V. V.; Troyanov, S. I.; Letov, A. V.; Strunkina, L. I.; Minacheva, M. Kh.; Furin, G. G.; Rosenthal, U.; Shur, V. B. *J. Organomet. Chem.* **2000**, *598*, 243.

(56) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Letov, A. V.; Lyssenko, K. A.; Korlyukov, A. A.; Strunkina, L. I.; Minacheva, M. Kh.; Shur, V. B. *Organometallics* **2001**, *19*, 4072.

Scheme 28



only one ortho fluorine atom of a $B(C_6F_5)_3$ group is coordinated to the titanium atom. On reaction with acetone $CpTi[\eta^5\text{-}C_5H_4B(C_6F_5)_3]$ gave the zwitterionic adduct $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti(Me_2CO)$, wherein the molecule of acetone is bonded to the Ti(III) center through the oxygen atom.[56] In this adduct only one ortho fluorine atom of a $B(C_6F_5)_3$ group is coordinated to the metal.

Fullerene. The reaction of complex **1** with an equimolar amount of fullerene-60 in toluene at room temperature gave the first fullerene complex of titanium, $Cp_2Ti(\eta^2\text{-}C_{60})$ (Scheme 28).[57]

An X-ray diffraction study of this complex showed that it has the structure of a titanacyclopropane derivative, which should have a high potential for further derivatization reactions of the fullerene.

Examples of Catalytic Reactions

The complexes $Cp'_2M(L)(\eta^2\text{-}Me_3SiC_2R)$ are well suited as precatalysts for many reactions.[29] By using different Cp′ (Cp, Cp*, EBTHI) ligands, an additional ligand L (THF, pyridine, acetone), and substituents R with the metals (Ti, Zr), a fine-tuning of the catalytic reactions of these complexes was feasible, as mentioned above for the stoichiometric reactions. Here only the use of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ as a precatalyst is described.

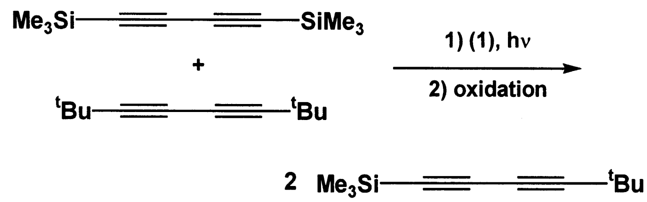
Polymerization of Acetylene. Efficient polymerization of acetylene was effected at 20−60 °C using the complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ as precatalyst.[58] The yield and the configuration of the resulting polyacetylene depended strongly on the solvent used. *trans*-Polyacetylene was exclusively formed in pyridine with a yield of 3300 mg of polyacetylene/mmol of titanium at 60 °C. A new mechanism was proposed and some deactivation processes investigated (see above and ref 32).[29c]

Oligomerization of 1-Alkynes. In contrast to the corresponding $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which is an excellent catalyst for the head-to-tail dimerization of terminal 1-alkynes such as 1-hexyne, the Cp complex **1** in this reaction gave only di- and trisubstituted benzenes.[59]

Isomerization and Intermolecular Hydrogen Transfer with Olefins. 1,5-Hexadiene, $H_2C{=}CHC_2H_4\text{-}CH{=}CH_2$, was isomerized at room temperature by complex **1** to 2,4-(*E*,*E*)- and 2,4-(*E*,*Z*)-hexadiene.[60] 1,4-Cyclohexadiene was isomerized by complex **1** at 60 °C to 1,3-cyclohexadiene, but a competitive reaction occurred, the hydrogen transfer yielding benzene and cyclohexene. 2-Hexene, $MeCH{=}CHC_3H_7$, was not isomerized by complex **1** to 1- or 3-hexene, nor was the cis:trans ratio changed. No olefin complexes or coupling products were obtained. 1-Hexene, $C_4H_9CH{=}CH_2$, was isomerized to *cis*-2-hexene and *trans*-2-hexene by complex **1** in accordance with the factors governing their thermodynamic stability. At the end of the reaction the alkyne complex **1** was recovered nearly quantitatively. No olefin complexes or coupling products were obtained.[60]

(57) Burlakov, V. V.; Usatov, A. V.; Lyssenko, K. A.; Antipin, M. Yu.; Novikov, Yu. N.; Shur, V. B. *Eur. J. Inorg. Chem.* **1999**, 1855.
(58) Ohff, A.; Burlakov, V. V.; Rosenthal, U. *J. Mol. Catal.* **1996**, *108*, 119.
(59) (a) Varga, V.; Petrusova, L.; Cejka, J.; Hanus, V.; Mach, K. *J. Organomet. Chem.* **1996**, *509*, 235. (b) Stepnicka, P.; Gyepes, R.; Cisarova, I.; Horacek, M.; Kubista, J.; Mach, K. *Organometallics* **1999**, *18*, 4869 and references therein.

Scheme 29



Photocatalytic C−C Single-Bond Metathesis. UV irradiation of a 1:1 mixture of the butadiynes ${}^tBuC{\equiv}CC{\equiv}C{}^tBu$ and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ in toluene with 4 equiv of **1** afforded, after oxidative workup, the unsymmetrically substituted diyne ${}^tBuC{\equiv}CC{\equiv}CSiMe_3$, in addition to the symmetrically substituted starting diynes (Scheme 29).[61] Since the workup was not optimized and is associated with a certain degree of decomposition of the three butadiynes, the yield of ${}^tBuC{\equiv}CC{\equiv}CSiMe_3$ was only 5%.

This reaction does not proceed in the absence of **1**. Both thermal (100 °C) and photochemical activation at the same time are essential for this first titanocene-mediated, photocatalyzed C−C single-bond metathesis in homogeneous solution. This metathesis is not a catalytic process, because an excess of the diynes favors the above-mentioned coupling reactions (similar to those shown in Schemes 12 and 13).[36a] The course of the reaction can be formulated in terms of a reaction of **1** with ${}^tBuC{\equiv}CC{\equiv}C{}^tBu$ to give the binuclear complex with an intact C_4 backbone and with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ to give the σ,π-alkynyl-bridged cleavage product.

Under the influence of light both 2:1 complexes then are subsequently cleaved to form the extremely unstable monomeric Ti(III) complexes $[Cp_2Ti(\sigma\text{-}C{\equiv}C{}^tBu)]$ and $[Cp_2Ti(\sigma\text{-}C{\equiv}CSiMe_3)]$, which then react to produce either the respective starting complexes or the unsymmetrically substituted binuclear complex (Scheme 30).

This reaction was checked by ^1H NMR experiments, which gave, after mixing the isolated symmetrical 2:1 complexes and irradiation at 100 °C, in 21% yield the unsymmetrical binuclear complex. The reverse reaction is realizable as well: i.e., photolysis of ${}^tBuC{\equiv}CC{\equiv}CSiMe_3$ complexes.

Hydrosilylation of Schiff Bases. Complex **1** was found to be a suitable precatalyst for the hydrosilylation

(60) Ohff, A.; Burlakov, V. V.; Rosenthal, U. *J. Mol. Catal.* **1996**, *105*, 103.
(61) (a) Kirchbauer, F. G.; Pulst, S.; Heller, B.; Baumann, W.; Rosenthal, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 1925. (b) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112.

Scheme 30

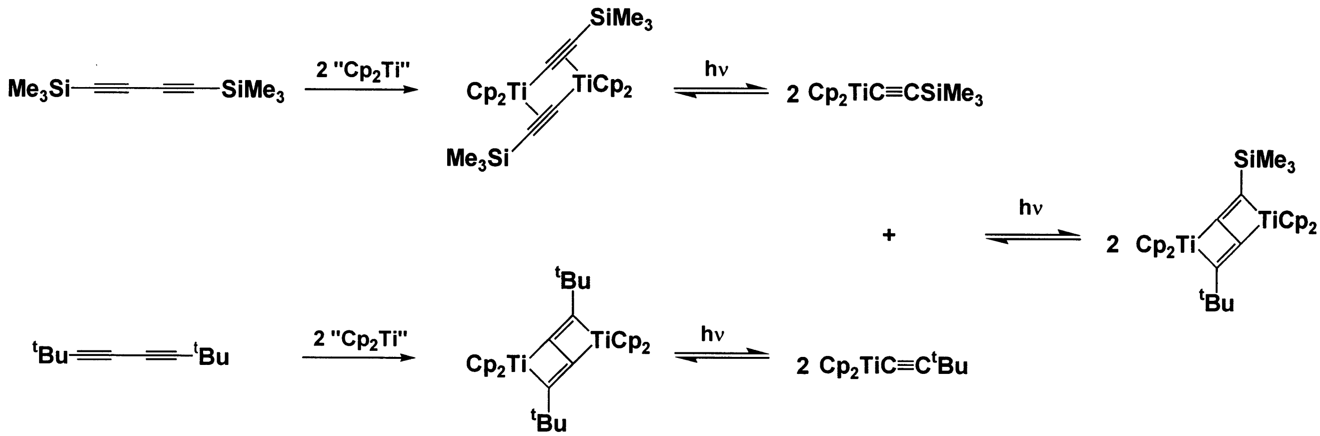


Table 3. Selected 1-Hetero Cyclopropenes "$L_nHet(\eta^2\text{-}Me_3SiC_2SiMe_3)$"

	$(\eta^5\text{-}C_5H_5)_2$-Ti[8,10b,28]	$(\eta^5\text{-}C_5Me_5)_2$-Ti[9,10b,28]	{HC[(CMe)-NAr)]$_2$}Al[68b]	(i-Pr)$_2$Si[71a]
		^{13}C NMR		
$\delta(C_2)$ (ppm)	244.7	248.5	228.5	no data[a]
		X-ray		
$d(C_2)$ (Å)	1.283(6)	1.3098(4)	1.382(4)	1.324(3)
d(C−Het)	2.136(5)	2.122(3)	1.899(3)	1.866(2)
(Å)	2.139(4)	2.126(3)	1.908(3)	1.861(2)
C−C−Si	141.6(3)	134.8(3)	133.7(2)	140.0(2)
(deg)	145.7(4)	136.8(3)	134.0(2)	140.8(2)

[a] For the corresponding Me_2Si compound, 189.6 ppm.[3b]

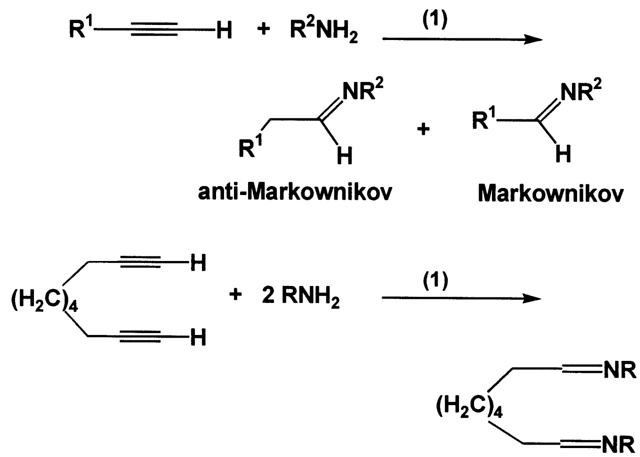
of aldimines and ketimines with Ph_2SiH_2.[62] Aldimines such as PhCH═NMe and PhCH═NCH_2Ph were hydrosilylated, but not PhCH═NPh. Also the ketimines Ph_2C═NH, Me(^{n}Bu)C═NCH_2Ph and Me(Cy)C═NCH_2-Ph, but not MePhC═NPh, underwent hydrosilylation.

Dehydrocoupling of Hydrosilanes. Harrod was the first who used titanocene and zirconocene dimethyl compounds, Cp_2MMe_2, as catalysts for polycondensation reactions of hydrosilanes.[63a,b] Complex **1** is a catalyst for oligomerization of hydrosilanes ($PhMeSiH_2$, 22% dimer, 27% trimer, 9% tetramer; Ph_2SiH_2, 42% dimer) and polymerization ($PhSiH_3$, $M_w = 1760$) also.[64a] Disilanes such as H_2(Me)SiSi(Me)H_2, H_2(Ph)SiSi(Me)H_2, and H_2(Ph)SiSi(Ph)H_2 were investigated in the dehydrocoupling reaction, catalyzed by **1**.[64b] In the first step of the oligomerization the disilanes are cleaved and, after 2 days, starting from H_2(Me)SiSi(Me)H_2, a completely insoluble cross-linked polymethylsilane was obtained. From H_2(Ph)SiSi(Ph)H_2 triphenyltrisilane was formed, in addition to the disproportionation products Ph_2SiH_2 and Ph_2(H)SiSi(Ph)H_2.

Ring-Opening Polymerization. Complex **1** was tested as a precatalyst for the catalytic ring-opening polymerization of lactams. In the case of β-propiolactam in refluxing toluene polymerization occurred, whereas with ϵ-caprolactam only the above-mentioned formation of a Ti(III) complex (Scheme 22) was observed.[51] There are some good arguments to assume similar lactamate complexes as reactive intermediates in the ring-opening polymerization of β-propiolactam, because this complex should be able to insert further lactam.

ϵ-Caprolactone was polymerized by complex **1** with a TON (turnover number) of 4270,[65] but the above-mentioned bimetallic complex $[Cp_2Ti](\mu\text{-}\eta^1\text{:}\eta^2\text{-}Me_3SiCCSiMe_3)(\mu\text{-}H)[Al(^iBu)_2]$, obtained from complex **1** and diisobutylaluminum hydride (Scheme 25), was found to be much more active, giving a polymer with a TON of 43 000.[53]

Scheme 31



Hydroamination. First experiments had shown that complex **1** is a useful precatalyst for the hydroamination of $Me_3SiC{\equiv}CH$ and PhC≡CH with $PhNH_2$.[66] More recently, the hydroamination of PhC≡CPh and PhC≡CMe, as well as the anti-Markownikow hydroamination of terminal alkynes, RC≡CH and HC≡C$(CH_2)_2$C≡CH, with a series of amines RNH_2 using complex **1** as catalyst was reported to afford high yields of the desired products (Scheme 31).[67]

General Remarks

As mentioned in the Introduction, the titanocene fragment Cp_2Ti: is isolobal with the dialkylsilylene R_2-

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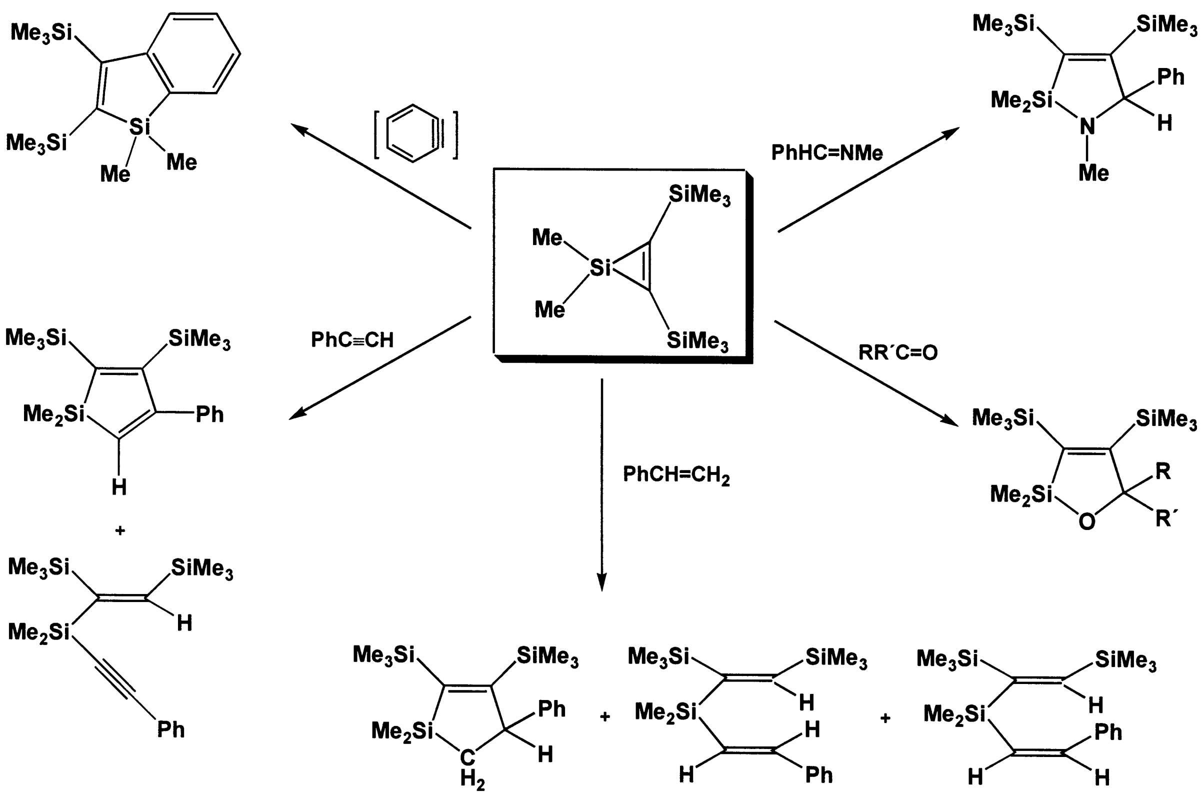
Scheme 32



Si: (and also with R_2C:, RAl:, RB:, RN:, etc.).[68a] This is why the 1-hetero-cyclopropenes, formed in reactions of these low-valent units with alkynes, are sometimes similar to each other with respect to their structures and reactivity. Only selected examples for this are discussed to illustrate these similarities, alluded to in the Introduction.

Spectroscopic and Structural Data. Some spectroscopic and structural data of selected 1-hetero-cyclopropenes "$L_nHet(\eta^2$-$Me_3SiC_2SiMe_3)$" with Me_3Si substituents are compared in Table 3.

Calculations concerning the stabilizing electron delocalization effects in 1-silacyclopropenes initially claimed by Vol'pin[1] suggest that there is none[69a] or only a very weak effect in this direction.[69b,c] To the best of our knowledge there are no such calculations on this point of view for 1-titanacyclopropenes.[39c]

Reactivity. In a series of papers Seyferth and coworkers reported that 1-silacyclopropenes such as 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene are hyperreactive toward unsaturated C═O, C═C, C≡C, C═N, etc. bonds, giving by insertions mostly five-membered cyclic products (Scheme 32).[70]

It has been pointed out that this behavior is typical also for the titana- and zirconacyclopropenes (see Introduction and Scheme 5).[29] It is worth mentioning that such isostructural products are formed mostly by starting from $Cp^*_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$ and $Cp^*_2Zr(\eta^2$-$Me_3SiC_2SiMe_3)$ complexes, whereas for $Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$ the tendency for dissociation of the alkyne is predominant.

Different 1-silacyclopropenes are known to be good photochemical precursors of silylenes.[71b] Such an elimination reaction of the alkyne, described in this paper for 1-titanacyclopropenes, also was observed in the reaction of the 1,1-dimesityl-2-trimethylsilyl-3-phenylsilirene: $Me_3SiC≡CPh$ was eliminated to give the free R_2Si: fragment, which reacted with $Me_3SiC≡CC≡CSiMe_3$ that was present, forming the 1,1-dimesityl-2-((trimethylsilyl)ethynyl)-3-(trimethylsilyl)silirene (Scheme 33).[72]

Weidenbruch described the products, obtained by reaction of 1,3-diynes and silylenes (Scheme 33), as isostructural to the binuclear complexes with intact C_4 units between the two titanium centers in which the former diynes are transformed to "zig-zag butadiene ligands" or μ-$\eta(1-3)$:$\eta(2-4)$-*trans*,*trans*-tetradehydrobutadiene moieties between two metallocene cores (see above).[73] Such structures, never found for Zr–Zr,[38a,41] were realized with Ti–Ti[35] and Si–Si[73] homo-combinations as well as the Ti–Si[43a,b] and Zr–Si[43a,c,d] hetero-

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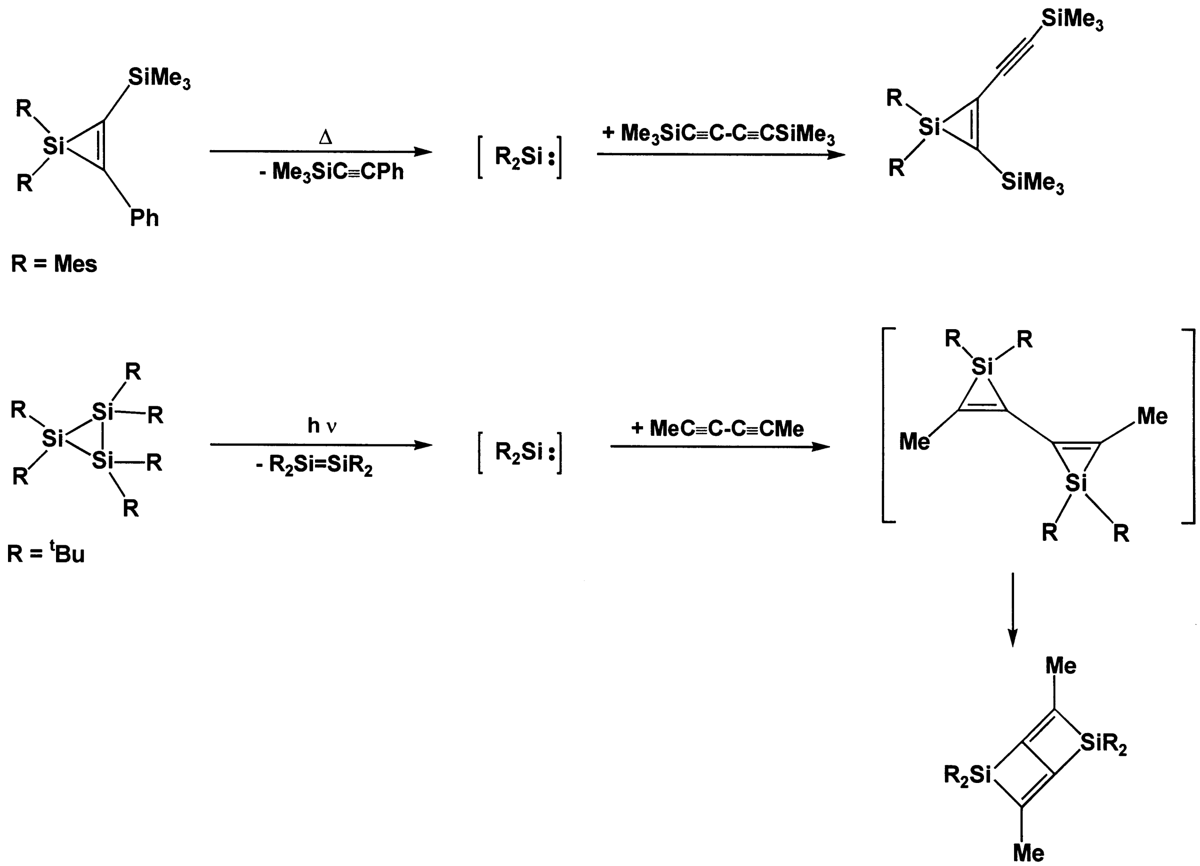
Scheme 33



mixtures (Scheme 15). This example nicely illustrates that the similar reactivities of "silacarbenes" and "metallocenes" are not restricted to alkynes only.

Conclusion

The spectroscopic and structural data of the complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**), as a stable titanocene–alkyne complex without additional stabilizing ligands, justify the bonding description as a 1-titanacyclopropene. Examples for stoichiometric and catalytic reactions indicate its high reactivity toward unsaturated substrates. Together with similar complexes, it offers a number of compelling advantages over other widely used titanocene-generating systems (as found also for zirconium[15c]).

(a) Complex **1** is very easily prepared in large quantity directly from the commercially available Cp_2TiCl_2, magnesium, and bis(trimethylsilyl)acetylene. It is stable at room temperature and can be stored for a long time under an inert atmosphere.

(b) The sole side product of the reaction, bis(trimethylsilyl)acetylene, is soluble and volatile and thus easy to remove from the reaction products and can be recycled.

(c) The complex allows reactions in a broad variety of solvents, in particular nonpolar solvents such as saturated hydrocarbons.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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