Bis(trimethylsilyl)acetylene Complexes of Titanocenes and Zirconocenes: Their Recent Chemistry and Reactions with Lewis Acids

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Dedicated to Prof. Dr. Dirk Walther on the occasion of his 65th birthday[‡]

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The chemistry of the metallocene bis(trimethylsilyl)acetylene complexes $[Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ [M = Ti, without L (**1**); M = Zr, L = THF (**2a**); M = Zr, L = pyridine (**2b**)], the pentamethylcyclopentadienyl complexes $[Cp^{\star}_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ [M = Ti (**3**), Zr (**4**)], and the ethylenebis(tetrahydroindenyl) (ebthi) complexes *rac*-$[(ebthi)M(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ [M = Ti (**5**), Zr (**6**)] has been described in several reviews. A fine-tuning of the reactions is possible by varying the Cp ligands (Cp, Cp*, ebthi), additional the co-ligands (THF, pyridine), and/or metals (Ti, Zr), and it has been pointed out that these complexes offer a number of compelling advantages over other, similar, widely used metallocene reagents. In this microreview recent (2000–2004) examples of the chemistry of complexes **1**–**6** are summarized, and some special interactions with Lewis acids are described. In these reactions the metallocene cores "Cp'_2Ti" and "Cp'_2Zr" (Cp′ = substituted Cp ligands) are mostly formed after dissociation of the alkyne. As examples of this, a new selective zirconocene coupling route to large, functionalized macrocycles has been established from **2b** and polyynes, complex **1** catalyses the first anti-Markovnikov hydroamination of terminal alkynes, complexes **1** and **3** selectively form polynuclear titanium complexes by C–C coupling of N-containing heterocycles, and complexes **1**, **2b**, **3**, and **6** promote selective C–H and C–F bond-cleavage reactions of fluorinated N-containing heterocycles. Beside this recent chemistry, this microreview also focuses on the reactions of the above-mentioned complexes with the Lewis acids diisobutylaluminum hydride and tris(pentafluorophenyl)borane. For example, complexes **1**, **2b**, and **6** react with iBu_2AlH to give heterodimetallic complexes containing tetracoordinate planar carbon atoms. The titanium complex **1** reacts with $B(C_6F_5)_3$ with elimination of the alkyne and gaseous hydrogen to give an electrophilic substitution of the Cp or Cp* ligand in which zwitterionic Ti^{III} complexes are formed. The zirconium complexes **4** and **6** do not liberate hydrogen in the reaction with $B(C_6F_5)_3$, although, after C–H activation of one methyl group of the Cp* or Cp part of the ebthi ligand and a B–C bond formation, zwitterionic complexes containing alkylidene groups with agostic interactions with the metal center are obtained. Complex **5** reacts with $B(C_6F_5)_3$ with Si–C bond cleavage of the alkyne and formation of an alkynylboranate $[Me_3SiC{\equiv}CB(C_6F_5)_3]^-$, which is complexed by the "*rac*-(ebthi)Ti" fragment to give a zwitterionic complex. Some of the formed heterodinuclear complexes and the zwitterionic complexes are active catalysts in the ring-opening polymerization of lactones, cyclic carbonates, and epoxides, as well as the polymerization of ethylene.

Introduction

Coordinatively and electronically unsaturated complex fragments are often required to realize stoichiometric and catalytic reactions of organometallic compounds. These core complexes coordinate to the substrates, activate them, and push them in the direction of the desired products. This is nicely illustrated in manifold reactions of the complex fragments titanocene "Cp_2Ti" and zirconocene "Cp_2Zr" as unstable 14-electron compounds with a d^2 configuration (M^{II}). The possible interactions between occupied and unoccupied orbitals explain why these "Cp_2M" metallocenes react with a variety of unsaturated compounds to form metallacycles, having with a high potential to undergo diverse conversions with further substrates. An important question in this context is what ligand can be used that sufficiently stabilizes the metallocene fragment but is re-

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leased under mild conditions to generate the unstable and very reactive metallocene core.

Many systems are known to generate titanocene "Cp_2Ti" or zirconocene "Cp_2Zr" very well. Selected examples are mixtures of [Cp_2ZrCl_2] with *n*BuLi, which form [$Cp_2Zr(\pi$-n-butene)] via [$Cp_2Zr(\sigma$-*n*Bu$)_2$], and the reaction of [Cp_2ZrCl_2] with EtMgCl, which forms [$Cp_2Zr(\pi$-ethylene)] via [$Cp_2Zr(\sigma\text{-Et})_2$]. In some cases these complexes are stabilized by additional ligands, such as those found in the complexes [$Cp_2Zr(PR_3)(\pi$-*n*-butene)] or [$Cp_2Ti(PMe_3)(\pi$-ethylene)]. Other complexes like [$Cp_2Ti(PMe_3)_2$] and [$Cp_2Zr(\pi$-1,3-butadiene)] can also be used. This chemistry has been summarized in a number of excellent reviews and various informative contributions in textbooks.[1−15]

The applicability and the success of these systems often depends on their preparative accessibility, on the selectivity of the conversions, and on the inertness of the stabilizing ligands. From this point of view, all of the above -mentioned systems have certain disadvantages. Nevertheless, they have been frequently and successfully used for organic synthesis over the few last years.

We have described the stable and well-defined metallocene bis(trimethylsilyl)acetylene complexes [$Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$] [M = Ti, without L (**1**); M = Zr, L = THF (**2a**); M = Zr, L = pyridine (**2b**)], the pentamethylcyclopentadienyl complexes [$Cp^*{}_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$] [M = Ti (**3**), Zr (**4**)], and the ethylenebis(tetrahydroindenyl) complexes *rac*-[(ebthi)$M(\eta^2\text{-}Me_3SiC_2SiMe_3)$] [M = Ti (**5**), Zr (**6**)] as novel reagents for this type of chemistry (Scheme 1). All these complexes are synthesized under anaerobic conditions by the reaction of the corresponding dichlorides [Cp'_2MCl_2] (Cp′ = substituted Cp; M = Ti, Zr) with magnesium in THF at room temperature in the presence of bis(trimethylsilyl)acetylene.[16−25]

The chemistry of these complexes, and particularly their bonding situation, their spectroscopic properties, their reactivity and mechanistic behavior etc., has been described in several reviews.[16−25] Variation of the Cp ligands (Cp, Cp*, ebthi), additional the co-ligands (THF, pyridine) and/or the metals (Ti, Zr) enables a fine-tuning of their reactivity. It has been pointed out that these complexes offer a number of compelling advantages over other widely used

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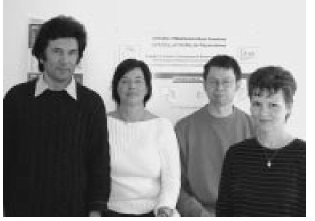

Vladimir V. Burlakov (left) was born in Moscow in 1955. He graduated from the M.V. Lomonosov Moscow Institute of Fine Chemical Technology in 1982. Since 1982, he has been working at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). In 1995, he received his Ph.D. degree with M. E. Vol'pin and V. B. Shur. Since 1992, he has often been a visiting research scientist in Rostock, hosted by the Rosenthal group. His scientific interests are focused on the transformation of unsaturated hydrocarbons and small molecules mediated by metal complexes of Group IV.

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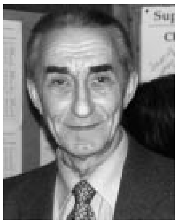
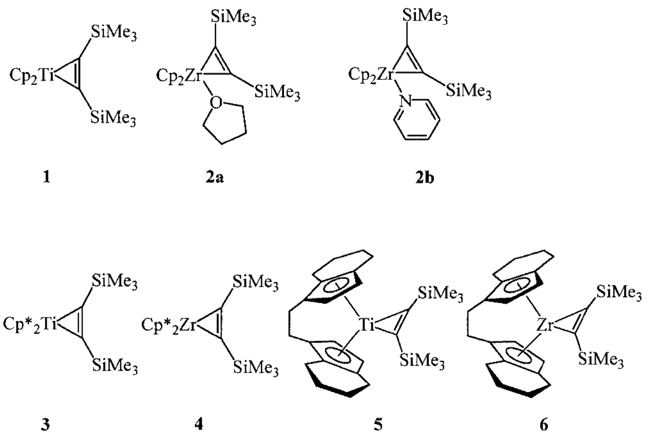
Wolfgang Baumann (center right), born in 1962 in Zweibrücken (Palatinate), studied chemistry at the University of Kaiserslautern (1982−1988), obtained his Diploma there in 1988, and did his doctoral work in the group of C. G. Kreiter (preparative organometallic chemistry: photochemistry of carbonyl-cyclopentadienyliron compounds). After graduation in 1990 he became "scientific coordinator" at the "Graduiertenkolleg" Chemical Reactivity and Molecular Order at the University of Siegen (1990−1991) and did postdoctoral work (organolithium chemistry, solid-state NMR) in the group of H. Günther (1991−1993). He has since worked in the Max Planck Research Group "Complex Catalysis" at the University of Rostock (1993−1996), the Institute of Organic Catalysis Research (1997−2002), and the Leibniz Institute of Organic Catalysis at the University of Rostock (from 2003).

Anke Spannenberg (right), born in 1967 in Rostock, Germany, studied chemistry and mathematics at the College of Education in Güstrow (1985−1990), graduated (Dr. rer. nat.) in 1994 under the supervision of H.-J. Holdt at the University of Rostock, and became a member of the Max Planck Research group "Complex Catalysis" at the University of Rostock (1995−1996). As a research scientist she has been working at the Institute of Organic Catalysis Research (1997−2002) and since 2003 at the Leibniz Institute for Organic Catalysis at the University of Rostock. Her scientific interests focus on X-ray crystal structure analysis.



Vladimir B. Shur was born in Moscow in 1936. He graduated from the Moscow Institute of Chemical Technology in 1959. From 1959 to 1962, he worked in industry. Since 1962 he has been working at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). In 1972, he received his Ph.D. degree with M. E. Vol'pin. From 1964 to 1989, he was head of the research group on nitrogen fixation in the Laboratory of Complex Organometallic Catalysts, headed by M. E. Vol'pin. In 1989, he received his degree of Doctor of Chemical Sciences. In the same year, he became head of the Laboratory of Metal Complex Activation of Small Molecules. Since 1991, he is Professor of Chemistry. His scientific interests focus on molecular nitrogen fixation, C−H bond activation, acetylene complexes of the Group IV metals, and coordination and catalytic chemistry of anticrowns.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.



Scheme 1

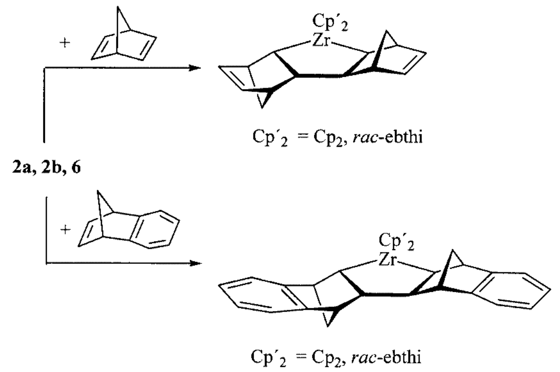
systems that significantly expand the scope of metallocene-based coupling reactions.[18]

In this microreview recent (2000−2004) examples of the chemistry of complexes **1−6** are summarized, and some special interactions with Lewis acids are described.

New Reactions

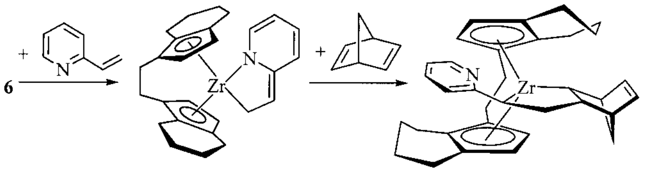
Two different reaction pathways for complexes **1−6** — coupling and elimination of the bis(trimethylsilyl)acetylene — represent the two most commonly found types of reactions of these complexes, with the latter one being the most attractive because of the generation of metallocenes.[18] The formation of stable substituted titanocenes by elimination of bis(trimethylsilyl)acetylene from the corresponding alkyne complexes has been documented in some excellent papers by Mach and coworkers.[26,27]

The reaction of **2a**, **2b**, or **6** with norbornadiene or benzonorbornadiene proceeds with elimination of the alkyne (and THF or pyridine) to give zirconacyclopentanes bearing additional functional groups (Scheme 2).[28] Note that in almost all reaction schemes the elimination of co-ligands and/or bis(trimethylsilyl)acetylene is omitted for simplicity.



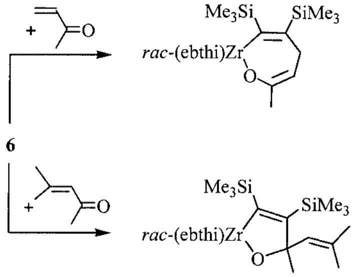
Scheme 2

Another substituted zirconacyclopentane has been isolated from the reaction of **6** with 2-vinylpyridine and norbornadiene. This complex is formed, via a 2-vinylpyridine complex intermediate,[29] by elimination of the bis(trimethylsilyl)acetylene and coupling of the coordinated pyridine and norbornadiene fragments (Scheme 3).[28]



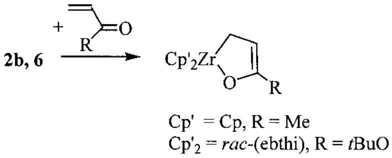
Scheme 3

Polar functionalized olefins also react with complexes **2b** and **6**, although in a different manner, to give either coupling products with the alkyne or substitution of the alkyne.[30] Complex **6** forms a novel 1,4-conjugated insertion product with methyl vinyl ketone, whereas mesityl oxide forms a zirconadihydrofuran by insertion of the carbonyl group (Scheme 4).



Scheme 4

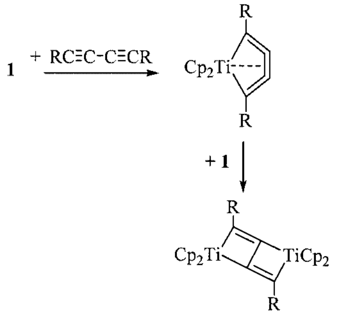
In contrast, **2b** and methyl vinyl ketone, or **6** and *tert*-butyl acrylate, eliminate the alkyne to yield a different zirconadihydrofuran (Scheme 5).



Scheme 5

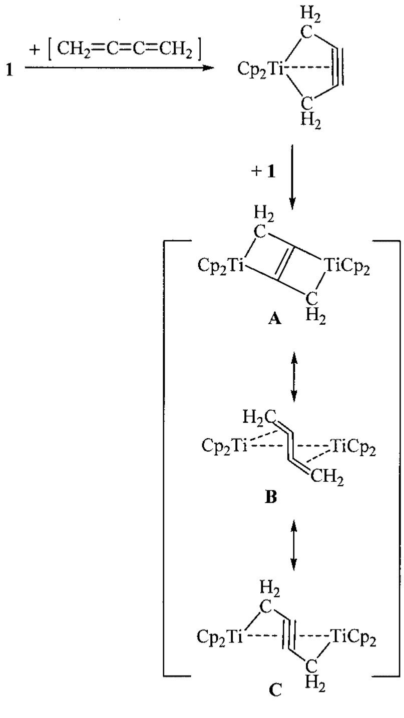
It is well known that the five-membered titanacyclocumulenes (1-titanacyclopenta-2,3,4-trienes), which can be considered formally as mononuclear "*cis*-diyne" complexes, are formed in the reactions of **1** with 1,3-butadiynes.[17] These compounds react, in the case of titanium, with further complex **1** to yield the dinuclear "*trans*-diyne" complexes with "zigzag butadiyne ligands" — μ-η(1,3),η(2,4)-

trans,trans-tetradehydrobutadiene moieties — between the two titanocene cores (Scheme 6).



Scheme 6

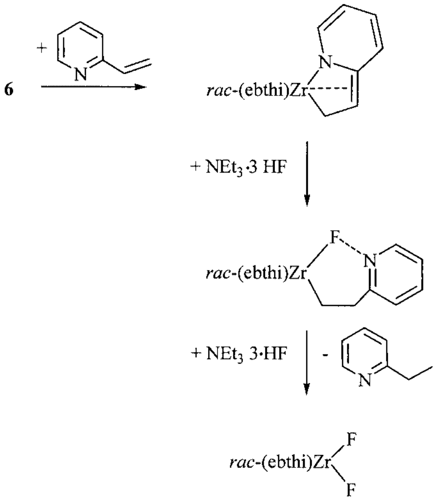
The novel reaction of 2 equiv. of **1** with 1,4-dichloro-2-butyne gives, probably by the formation of 1,2,3-butatriene, $[Cp_2TiCl_2]$, and $Me_3SiC_2SiMe_3$, 1-titanacyclopent-3-yne, formally a "*cis*-triene" complex, which reacts with additional **1** to give a "*trans*-triene" complex with bridging "zigzag butatriene ligands" between the two titanium centers (Scheme 7).[23,31] Its structure is best described as a 2,5-dititanabicyclo[2.2.0]hex-1(4)-ene (**A**) rather than the resonance structures B — a μ-*trans*-butatriene-bridged π-complex — or C — a butynediyl-bridged σ-propargylic complex (Scheme 7).



Scheme 7

Suzuki and coworkers have reported the complexation of 1,2,3-butatrienes with zirconocene with formation of the corresponding 1-zirconacyclopent-3-ynes.[32,33] Jemmis,[34] Lin,[35] and Jiao,[36] and their coworkers, have compared these rather exotic compounds by detailed calculations.

The zirconocene monofluoride *rac*-[(ebthi)Zr(F)-(CH_2CH_2-2-py)] and difluoride *rac*-[(ebthi)ZrF_2] have been obtained, via the 2-vinylpyridine complex *rac*-[(ebthi)Zr(2-vipy)], by reaction with triethylamine tris(hydrofluoride) (Scheme 8).[37]



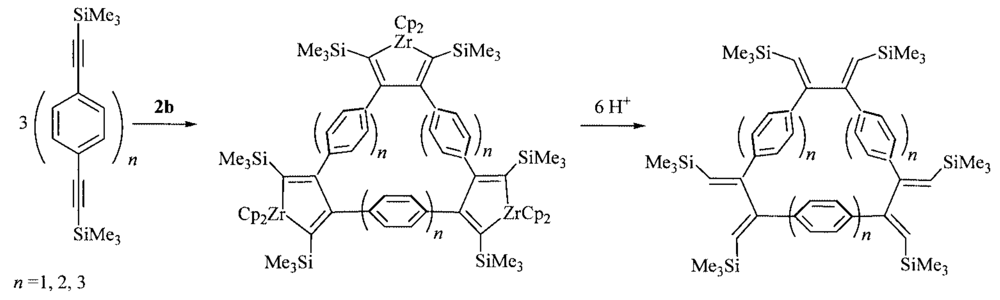
Scheme 8

This novel method for the synthesis of zirconocene difluorides and alkyl monofluorides via the 2-vinylpyridine complexes $[Cp'_2Zr(L)(2\text{-vipy})]$ has also been reported for other compounds of the type $[Cp'_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ with different ligand Cp'_2 systems, such as $(thi)_2$ [bis(η^5-tetrahydroindenyl)], $Me_2Si(\eta^5\text{-}C_5H_4)_2$ [dimethylsilylbis(η^5-cyclopentadienyl)], and ebthi.

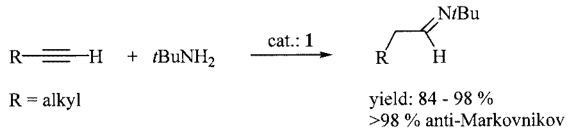
In the last few years several research groups have taken advantage of the above-mentioned complexes for stoichiometric and catalytic reactions. Tilley and coworkers have reported that the complex $[Cp_2Zr(pyridine)(\eta^2\text{-}Me_3SiC_2\text{-}SiMe_3)]$ (**2b**) is best suited for a new selective zirconocene-coupling reaction of polyynes to give large, functionalized macrocycles in which zirconacyclopentadienes are bridged by different groups.[38−40] Protolysis of these products gives the corresponding substituted butadienes. A large number of dimeric and trimeric bridged metallacycles have been synthesized by this method (Scheme 9) including, most recently, several substrates with fluoro substituents.[41]

Beller et al. have described the first anti-Markovnikov hydroamination of terminal alkynes with the complex $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**) as a precatalyst (Scheme 10).[42]

This complex was subsequently compared to the corresponding substituted complexes $[Cp'_2Ti(\eta^2\text{-}Me_3SiC_2\text{-}SiMe_3)]$ [Cp′ = Cp* (**3**) and C_5H_4Et], which need a higher reaction temperature.[43] Detailed theoretical calculations by Jiao have revealed that the experimentally observed regioselectivity is determined by the relative stability of the postulated intermediate π-complexes "$[CpTi(NH_2)(=NH)(\eta^2\text{-}HC{\equiv}CH)]$", in which the electrostatic substitution favors the Markovnikov product for aniline and the sterically repulsive destabilization disfavors the Markovnikov



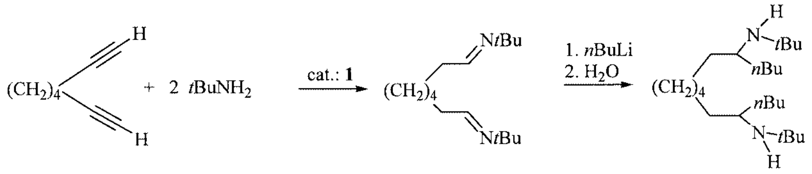
Scheme 9



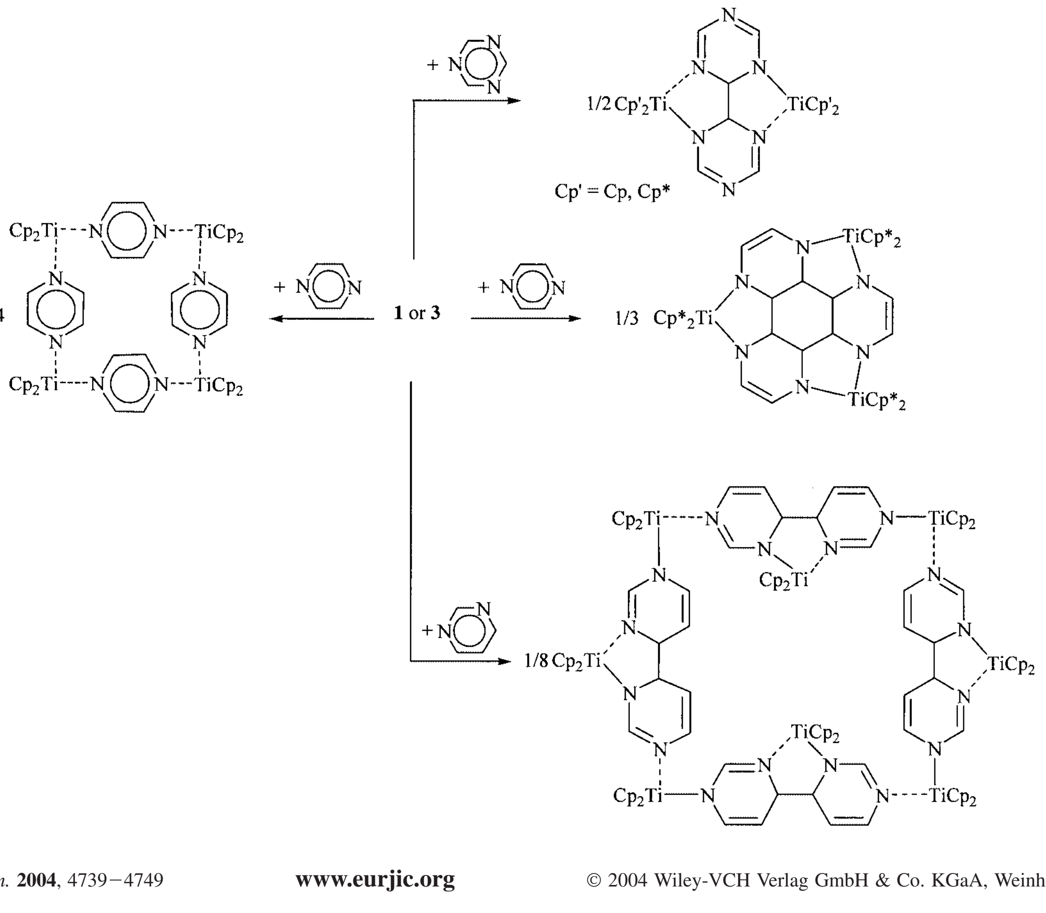
Scheme 10

product for *tert*-butylamine. The one-pot synthesis of several branched secondary aliphatic amines by the hydroamination of terminal alkynes with aliphatic primary amines in the presence of **3** gave the aldimines, in situ, which react with organolithium compounds to give the α-branched amines in high yields (Scheme 11).[44]

Odom and coworkers have compared the activity of complex **1** with a series of other titanium complexes as precata-



Scheme 11



Scheme 12

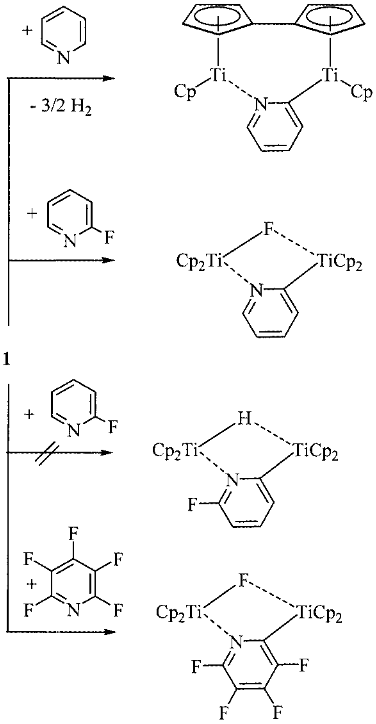
lysts for intermolecular alkyne hydroamination; they found that it has a lower activity than the commercially available $Ti(NMe_2)_4$.[45]

Beckhaus and coworkers have published very recently a series of excellent examples of molecular self-organization. The selective formation of polynuclear titanium complexes was realized in the reactions of **1** and **3** with different N-heterocyclic compounds[46,47] by directed reduction of six-membered nitrogen heterocycles and molecular self-organization (Scheme 12).

In these reactions, after dissociation of the bis(trimethylsilyl)acetylene from complexes **1** and **3**, the formed titanocene "Cp_2Ti" and permethyltitanocene "Cp^*_2Ti" moieties react in the same manner with triazine — by C−C bond coupling — to give dinuclear chelate complexes. However, different products were formed with pyrazine: a tetranuclear, pyrazine-bridged complex from **1**, and a trinuclear chelate complex, in a spontaneous threefold C−C coupling reaction, from **3**. Complex **1** gives an octanuclear complex with pyrimidine, whereas the reaction of **1** with triazine leads, by C−C coupling, to a dimeric chelate ligand.[46]

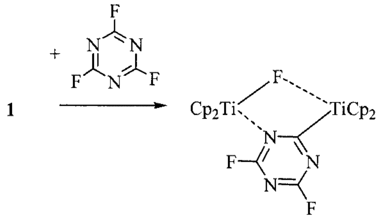
As discussed before for Tilley's reaction with [Cp_2Zr(pyridine)(η^2-$Me_3SiC_2SiMe_3$)] (**2b**),[38−41] the good solubility of the starting materials **1** and **3** allows a smooth separation of the in-most-cases sparingly soluble products. The bis(trimethylsilyl)acetylene formed from these reactions is soluble and volatile, and is thus easy to remove.

The crucial step of C−H activation has also been described by Beckhaus and coworkers for some reactions of complexes **1** and **3** with pyridine, fluorinated pyridines, and other N-containing heterocyclic compounds (Scheme 13).[47] Complex **1** and pyridine, for example, give a hydride-bridged dinuclear titanium fulvalene derivative after C−H activation, whereas monofluoropyridine reacts with **1**, by C−F activation, to give a fluoride-bridged dinuclear titanium complex. It is remarkable that no product resulting from a C−H activation was found in this case. Pentafluoropyridine reacts with **1** to give a similar perfluorinated product.



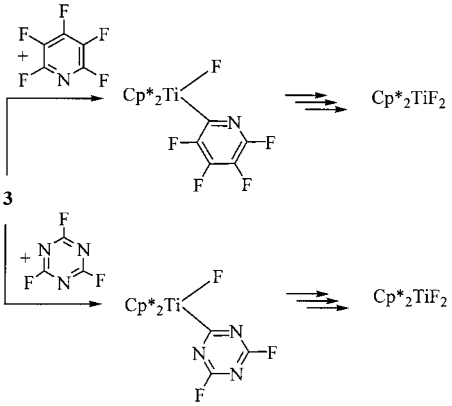
Scheme 13

A fluoride-bridged dinuclear titanium complex is formed in the reaction with 2,4,6-trifluoro-1,3,5-triazine by C−F activation (Scheme 14).



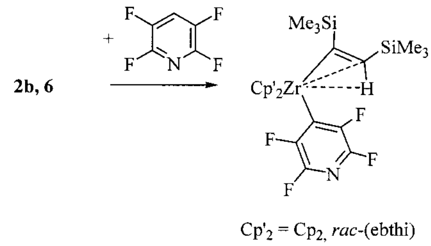
Scheme 14

The reaction of complex **3** with pentafluoropyridine or cyanuric fluoride forms, after C−F activation, mononuclear fluorotitanium(IV) complexes as intermediates, as proved by ^1H and ^{19}F NMR measurements, which go on to react with an excess of the substrates to give the difluoride [$Cp^*_2TiF_2$] (Scheme 15).



Scheme 15

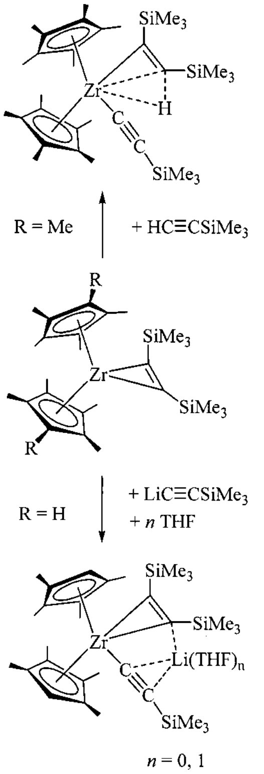
The corresponding zirconocene complexes **2b** and **6** behave completely differently in such reactions.[48] Tetrafluoropyridine reacts with **2b** or **6** by C−H activation to give 4-substituted pyridyl complexes that contain alkylidene groups with agostic interactions to the metal center (Scheme 16).



Scheme 16

This result is opposite to the above-mentioned titanium case in which C−F activation was preferred over C−H activation and the 2-position reacted. The reason for this could be a bimolecular reaction with precoordination of the N-atom of the pyridine and an attack of a second zirconocene in the 4-position. Such a coordination of the pyridine is impossible for complex **1**.

Mach and coworkers have recently described some reactions of substituted zirconocene complexes of bis(trimethylsilyl)acetylene with terminal acetylenes and lithium acetylides.[49] For example, complex **4** reacts with $HC{\equiv}CSiMe_3$ to give the agostic alkenyl-alkynyl complex $[Cp^*_2Zr\{\eta^3\text{-}[C(SiMe_3){=}CHSiMe_3]\}(\eta^1\text{-}C{\equiv}CSiMe_3)]$, as described before for the permethyltitanocene complex **3**. The corresponding complex $[(\eta^5\text{-}C_5HMe_4)_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ yielded the diamagnetic zirconate complex $Li[\{(\eta^5\text{-}C_5HMe_4)_2Zr\}\{\eta^1\text{-}(C{\equiv}CSiMe_3)\}\{\eta^2\text{-}(Me_3SiC{\equiv}CSiMe_3)\}]$ with $LiC{\equiv}CSiMe_3$ (Scheme 17).



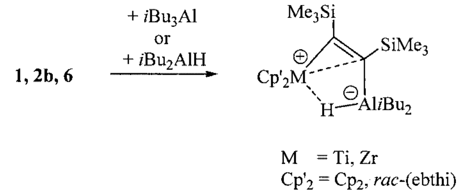
Scheme 17

New Reactions with Lewis Acids

One of the most remarkable discoveries during the past few decades was that the activity of metallocene-based Ziegler−Natta polymerization catalysts is based on cationic $[Cp'_2MR]^+$ complexes containing a metal atom in the +4 oxidation state. Such cationic moieties can easily be prepared by interaction of metallocene complexes $[Cp'_2MX_2]$ (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl, X = Me, CH_2Ph, H etc.) with strong Lewis acids (LA) such as $B(C_6F_5)_3$, Ph_3C^+ etc. After abstraction of X, the metallocenium ion-pair complexes with noncoordinating anions to give $[Cp'_2MX]^+[(\mu\text{-}X)\text{-}LA]^-$ complexes.

As well as the above-mentioned $[Cp'_2MX_2]$ complexes, the titana- and zirconacyclopropenes **1**−**6** also possess two M−C σ-bonds and their reactions with Lewis acids such as $B(C_6F_5)_3$, Al*i*Bu$_3$, and HAl*i*Bu$_2$ have been investigated in detail. The reaction of alkynyl- and alkenylmetallocene complexes with organoaluminum or -boron compounds has been intensively investigated by Erker[50] and Binger;[51] it leads to dimetallic systems of the type $[Cp_2M^1](\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}X)[M^2R^2_2]$ (M^1 = Zr, Hf, X = Cl, H, M^2 = Al, Ga; M^1 = Ti, X = H, M^2 = B) containing a planar-tetracoordinate carbon atom bridging between a group-4 transition metal and a main group element.

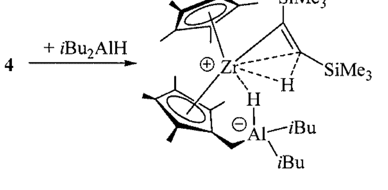
The reactions of the alkynyltitanocene and -zirconocene complexes **1**, **2b**, and **6** with Al*i*Bu$_3$ lead to similar heterodimetallic complexes, along with formation of isobutene and HAl*i*Bu$_2$.[52] These complexes are better prepared, however, by the direct reaction of the alkyne complexes with HAl*i*Bu$_2$ (Scheme 18).



Scheme 18

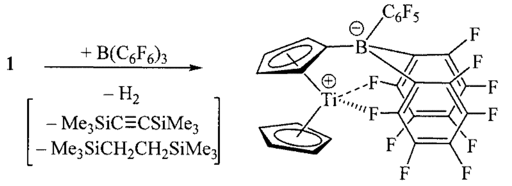
The X-ray crystal structure analyses of the complexes show planar, bicyclic, five-membered-ring systems containing the metal atom, the hydridic hydrogen, Al, C_β, and C_α. Some of these complexes are very active catalysts for the ring-opening polymerization of ε-caprolactone.[52]

Interestingly, the reaction of **4** with HAl*i*Bu$_2$ gave no such complexes. Instead, an electrophilic substitution of a hydrogen atom from one of the methyl groups of the Cp* ring by the HAl*i*Bu$_2$ moiety occurred.[53] No hydrogen or alkyne were liberated, and a product with an agostic σ-alkenyl group at the zirconium center and a μ-H atom between Al and Zr was isolated (Scheme 19).



Scheme 19

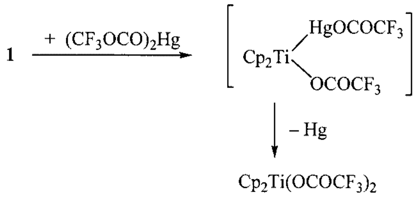
In the reaction of **1** with $B(C_6F_5)_3$ in toluene at room temperature the titanium(III) complex of $[TiCp\{\eta^5\text{-}C_5H_4B(C_6F_5)_3\}]$, a novel type of zwitterionic complex containing the $B(C_6F_5)_3$ group in the Cp ligand and no σ-bonded organic substituents at the titanium atom, was formed. Hydrogen, alkyne, and 1,2-bis(trimethylsilyl)ethane are liberated by the electrophilic substitution of a hydrogen atom of one of the η^5-C_5H_5 rings by a $B(C_6F_5)_3$ group (Scheme 20).[54,55]



Scheme 20

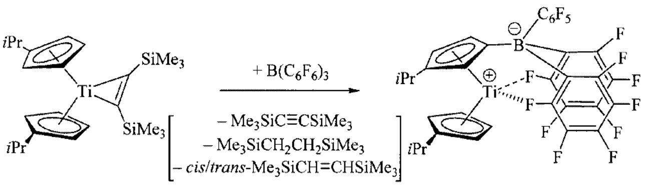
The reaction of $[Cp_2Ti(PhC_2SiMe_3)]$ with $B(C_6F_5)_3$ under the same conditions gives an identical product, but with a strongly diminished rate of reaction. The complex $[Cp_2Ti(PhC_2Ph)]$ does not react with $B(C_6F_5)_3$ at all under the same conditions, not even after one month. Thus, the replacement of the Me_3Si groups of the acetylene ligand by Ph substituents sharply decreases the reactivity of the corresponding acetylene complexes $[Cp_2Ti(R^1C_2R^2)]$ toward $B(C_6F_5)_3$.[56]

An attempt to electrophilically mercuriate the Cp rings in **1** by reaction with $Hg(OCOCF_3)_2$ was undertaken to obtain the complex $[TiCp(OCOCF_3)\{\eta^5$-$C_5H_4Hg(OCOCF_3)\}]$. It appeared, however, that the process proceeds in another way, and $[Cp_2Ti(OCOCF_3)_2]$ was isolated after the liberation of metallic mercury and alkyne (Scheme 21).[57]



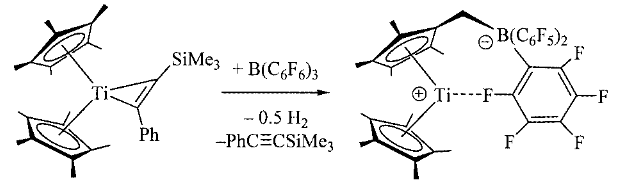
Scheme 21

The reaction of $[(\eta^5$-$i$$PrC_5H_4)_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)]$ with $B(C_6F_5)_3$ in toluene at room temperature also produces the zwitterionic titanium(III) complex $[Ti(\eta^5$-$i$$PrC_5H_4)\{\eta^5$-1,3-$i$$PrC_5H_3B(C_6F_5)_3\}]$ in which the 3-H atom of one of the C_5 rings has been substituted by a $B(C_6F_5)_3$ group (Scheme 22).[56] This complex is analogous in its structure to the titanium(III) zwitterion $[TiCp\{\eta^5$-$C_5H_4B(C_6F_5)_3\}]$ formed from the reaction of $B(C_6F_5)_3$ with **1** (Scheme 20). In this reaction, 1,2-bis(trimethylsilyl)ethene was also detected in addition to the silylated alkyne and 1,2-bis(trimethylsilyl)ethane. A characteristic feature of both zwitterionic complexes is the presence of coordinative bonds between the *ortho*-fluorine atoms of two C_6F_5 substituents and the positively charged titanium center.



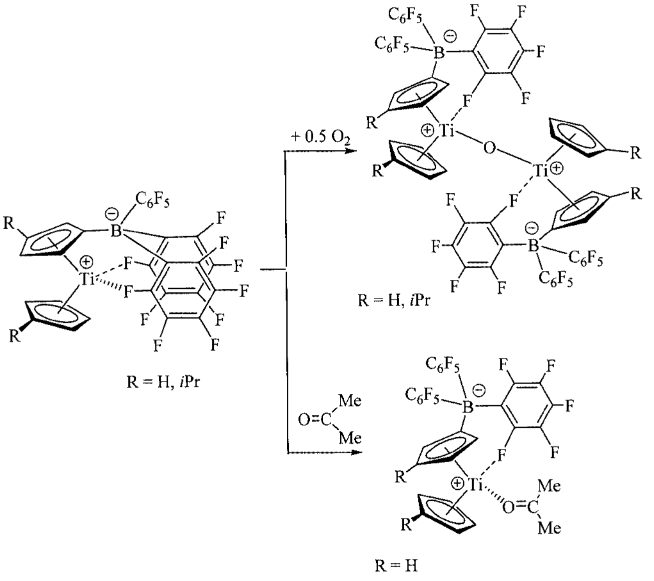
Scheme 22

An electrophilic substitution of a hydrogen atom of one of the methyl groups of the Cp* ring by a $B(C_6F_5)_3$ moiety was also found in the reaction of $B(C_6F_5)_3$ with $[Cp^*_2Ti(\eta^2$-$PhC_2SiMe_3)]$ — the zwitterionic Ti^{III} complex $[TiCp^*\{\eta^5$-$C_5Me_4CH_2B(C_6F_5)_3\}]$ was isolated (Scheme 23).[58]



Scheme 23

The oxidation of $[TiCp\{\eta^5$-$C_5H_4B(C_6F_5)_3\}]$ and $[Ti(\eta^5$-$i$$PrC_5H_4)\{\eta^5$-1,3-$i$$PrC_5H_3B(C_6F_5)_3\}]$ by atmospheric oxygen affords the isostructural zwitterionic titanoxanes $[Cp\{\eta^5$-$C_5H_4B(C_6F_5)_3\}Ti]_2(\mu$-O) and $[(\eta^5$-iPr$C_5H_4)\{\eta^5$-1,3-iPr$C_5H_3B(C_6F_5)_3\}Ti]_2(\mu$-O), respectively, which contain two zwitterionic units in the molecule (Scheme 24).[56] In each of these units only one *ortho*-fluorine atom of a $B(C_6F_5)_3$ group is involved in coordination to the titanium atom.

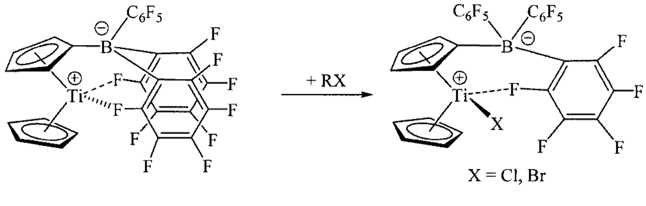


Scheme 24

These complexes are active catalysts for the cationic ring-opening polymerization of ε-caprolactone, THF, and propylene oxide, whereas γ-butyrolactone and 1-methyl-2-pyrrolidone are not polymerized under the same conditions.[59]

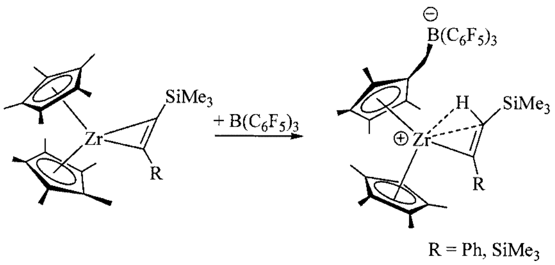
[TiCp{η^5-$C_5H_4B(C_6F_5)_3$}] also reacts readily with acetone to give the zwitterionic adduct [(Me_2CO)TiCp{η^5-$C_5H_4B(C_6F_5)_3$}], where the acetone is bonded to the Ti^{III} center through the oxygen atom and only one *ortho*-fluorine atom of the $B(C_6F_5)_3$ group is coordinated to the metal (Scheme 24).[56]

The monohalide complexes [TiXCp{η^5-$C_5H_4B(C_6F_5)_3$}] (X = Cl, Br) are produced by the reaction of [TiCp{η^5-$C_5H_4B(C_6F_5)_3$}] with alkyl halides (Scheme 25). A characteristic feature of the resulting complex is the coordination between one *ortho*-fluorine atom of one C_6F_5 group and the titanium center. As found for the zwitterionic titanoxanes, the chloride complex catalyses the cationic ring-opening polymerization of THF.[60,61]



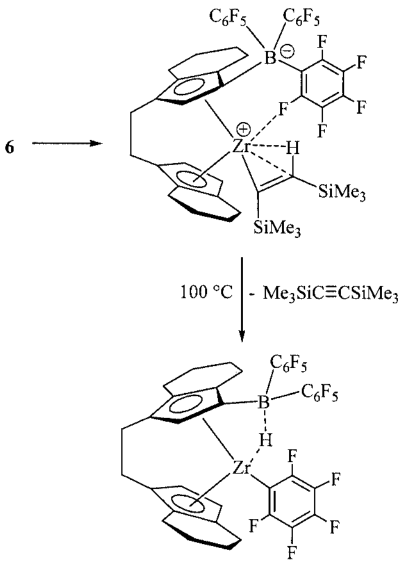
Scheme 25

The reactions of the corresponding zirconium complexes with $B(C_6F_5)_3$ differ from the reaction mode presented above. No hydrogen or alkyne are liberated in the reaction of [$Cp^*_2Zr(\eta^2$-$RC_2SiMe_3)$] (R = Ph, Me_3Si) with $B(C_6F_5)_3$ and the zwitterionic Zr^{IV} derivative [ZrCp*{η^5-$C_5Me_4CH_2B(C_6F_5)_3$}{C(R)=CH($SiMe_3$)}], which contains a σ-alkenyl group at the zirconium center, is produced (Scheme 26).[58]



Scheme 26

The reactions of the *rac*-ebthi complexes **5** and **6** with $B(C_6F_5)_3$ also proceed totally differently for Ti and Zr.[62] For **6** an electrophilic substitution of one H atom of the Cp ring in the 3-position occurs to give a zwitterionic alkenyl complex without liberation of hydrogen or alkyne (Scheme 27).

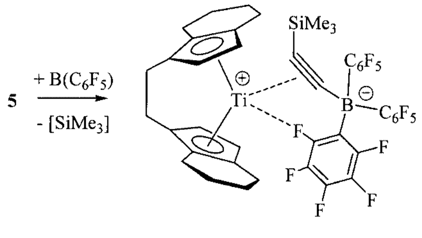


Scheme 27

When this complex is heated to 100 °C in solution the alkyne is eliminated and one B−C bond is cleaved, with a subsequent transfer of one C_6F_5 group from boron to zirconium, to give a complex with one μ-H atom between B and Zr (Scheme 27).

Both complexes are important for the understanding of deactivation processes in the polymerization of olefins and demonstrate the importance of the proper addition sequence when adding reagents in order to achieve catalytic activity. If **6** is first treated with ethene, the zirconacyclopentane formed is subsequently activated by $B(C_6F_5)_3$ to give a catalyst that is active for the polymerization of ethylene. However, if the borane is added to **6** first, neither the obtained complex nor the thermolysis product (Scheme 27) react with ethylene. Interestingly, the analogous complexes [ZrCp*{η^5-$C_5Me_4CH_2B(C_6F_5)_3$}{C(R)=CH($SiMe_3$)}] (R = Ph, $SiMe_3$; Scheme 26) are active in ethylene polymerization, presumably because they have no C−F interactions due to steric reasons.

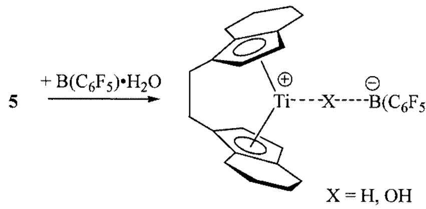
In the reaction of **5** with $B(C_6F_5)_3$ neither an electrophilic substitution of an H atom nor an elimination of the alkyne was observed. Instead, after substitution of one of the $SiMe_3$ groups in the coordinated bis(trimethylsilyl)acetylene by $B(C_6F_5)_3$, the first zwitterionic titanium(III) η^2-(trimethylsilyl)alkynylboranate complex *rac*-[{(ebthi)Ti}$^+$-{[η^2-$Me_3SiC_2B(C_6F_5)_3$]}−] was obtained (Scheme 28).



Scheme 28

In this complex the $[Me_3SiC_2B(C_6F_5)_3]^-$ ligand is unsymmetrically and weakly bonded to the Ti center by its C≡C bond as well as by one of the *ortho*-F atoms of the $B(C_6F_5)_3$ group. Complexes of alkynylboranates have not been isolated or characterized before, although they have frequently been postulated as reactive intermediates, for example in the $B(C_6F_5)_3$-catalyzed C−C coupling of alkynyl groups by bis(alkynyl)zirconocene(IV) complexes[63] and in the reaction of alkynylstannanes with boranes.[64]

Reaction of **5** with the Brönsted acid $B(C_6F_5)_3{\cdot}H_2O$ gives a mixture of the blue complexes $[rac\text{-(ebthi)Ti}]^+[HOB(C_6F_5)_3]^-$ and $[rac\text{-(ebthi)Ti}]^+[HB(C_6F_5)_3]^-$ (Scheme 29).[65]



Scheme 29

These complexes form a series of compounds of the type $[rac\text{-(ebthi)Ti}]^+[XB(C_6F_5)_3]^-$ with X = $Me_3SiC{\equiv}C$, OH, and H.

Conclusion

The reactions presented here show once again that the metallocene bis(trimethylsilyl)acetylene complexes $[Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ [M = Ti, without L (**1**); M = Zr, L = THF (**2a**); M = Zr, L = pyridine (**2b**)], the pentamethylcyclopentadienyl complexes $[Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ [M = Ti (**3**), Zr (**4**)], and the complexes *rac*-[(ebthi)M(η^2-$Me_3SiC_2SiMe_3$)] [ebthi = ethylenebis(tetrahydroindenyl); M = Ti (**5**), Zr (**6**)] offer a number of compelling advantages over other, widely used metallocene reagents as they are readily prepared directly from the dichlorides $[Cp'_2MCl_2]$, are stable at room temperature for a long time under argon atmosphere, and allow a control over the stoichiometry of reactions at elevated temperatures. The side-products of the reactions — bis(trimethylsilyl)acetylene, THF, and pyridine — are soluble and volatile and thus easy to remove. These complexes allow reactions in a broad variety of solvents, in particular nonpolar solvents such as pentane.

Acknowledgments

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