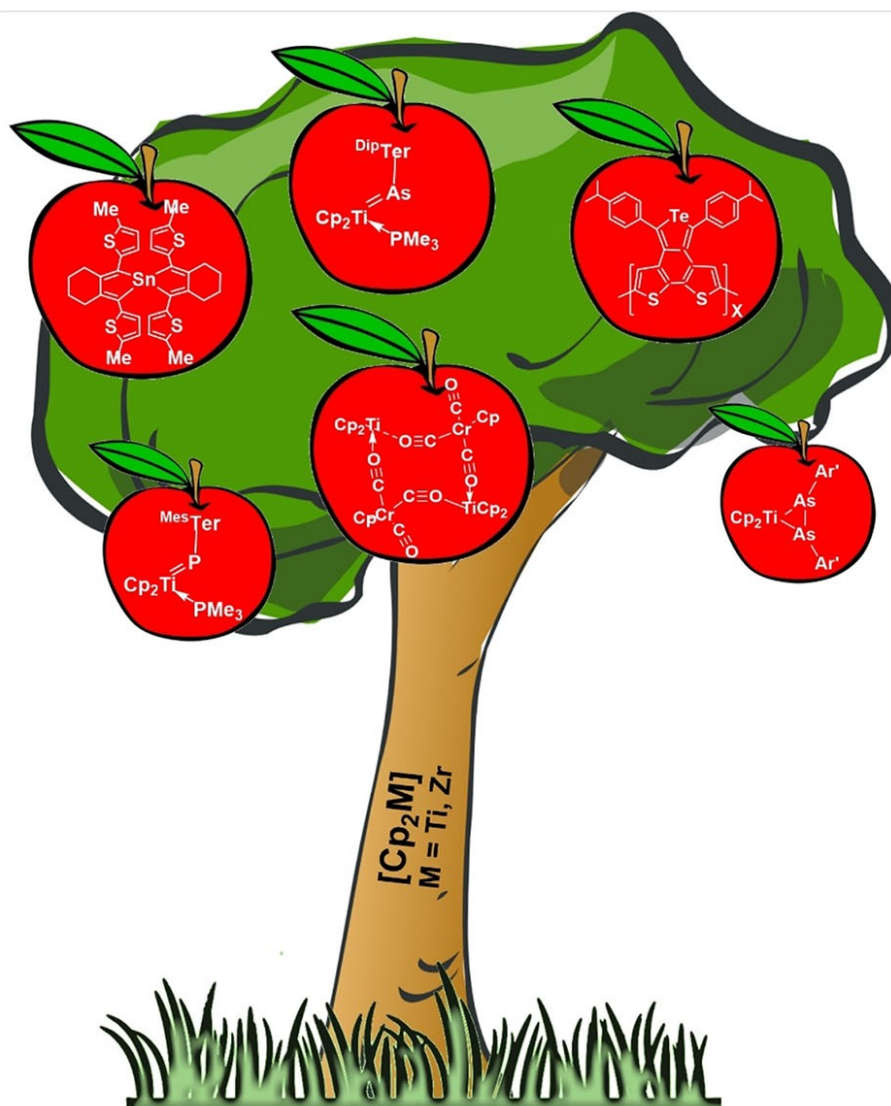


Latest News: Reactions of Group 4 Bis(trimethylsilyl)acetylene Metallocene Complexes and Applications of the Obtained Products

Uwe Rosenthal*^[a]

Dedicated to Dr. CSc. Karel Mach in recognition of his outstanding contributions to Organometallic Chemistry



Attractive – Active – Applications (as Apples 😊)

Recently published reactions of group 4 metallocene bis(trimethylsilyl)acetylene (btmsa) complexes from the last two years are reviewed. Complexes like $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with Cp' as Cp (cyclopentadienyl) and Cp^* (pentamethylcyclopentadienyl) have been considered ($\text{py} = \text{pyridine}$). These complexes can liberate a reactive low-valent titanium or zirconium center by dissociation of the ligands and act as “masked” M^{II} complexes ($\text{M} = \text{Ti, Zr}$). They represent excellent sources for the clean generation of the reactive coordinatively and electronically unsaturated complex

fragments $[\text{Cp}'_2\text{M}]$. This is the reason why they were used for many synthetic and catalytic reactions during the last years. As an update to several review articles on this topic, this contribution provides an update with recent examples of preparative organometallic and organic chemistry of these complexes, acting as reagents for a wide range of coordinating and coupling reactions. In addition, applications and investigations concerning reaction products derived from this chemistry are mentioned, too.

1. Introduction

In a recent example from a series of reviews,^[1] the question whether reactions of complexes such as $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{Cp}' = \text{Cp}$ as cyclopentadienyl and $\text{Cp}^* = \text{pentamethylcyclopentadienyl}$, $\text{py} = \text{pyridine}$, $\text{Me}_3\text{SiC}_2\text{SiMe}_3 = \text{btmsa}$, bis(trimethylsilyl)acetylene) could be considered as a part of a “Never ending story?” was raised.^[1f] This certainly seems true, as several examples have been added to this story in the relatively short timeframe of the last two years. Some older examples complete the summary, serving as a basis for an understanding of more recent ones. In addition, applications and studies of products obtained from this chemistry are mentioned. Applications, in this context, does not refer to industrial processes, but to the use of these complexes for synthetic purposes. New results for the attractive chemistry of $[\text{Cp}_2\text{Ti}^{\text{II}}]$ and $[\text{Cp}_2\text{Zr}^{\text{II}}]$ have been described in detail. Only parts of the relevant previous work in addition to the current development are briefly mentioned at the beginning of each chapter to show the basis for these extensions. Three distinct parts: (i) substitution reactions of $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ and coordination of other molecules; (ii) reactions of the new coordination compounds; and (iii) investigations and applications of the coordination compounds for chemical and physical purposes, constitute the main content of the recently published work summarized here. Often, there is overlap between these three areas.

2. Characterization of the Starting Complexes

In an older study, the question “Are Metallocene-Acetylene ($\text{M} = \text{Ti, Zr, Hf}$) Complexes Aromatic Metallacyclopropenes?” was discussed by Jemmis, Jiao and coworkers.^[2] Therein, the bonding situation for titanocene bis(trimethylsilyl)acetylene complexes $\text{Cp}_2\text{M}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ was investigated by comput-


ing the titanocene bis-silylacetylene complex $\text{Cp}_2\text{M}(\eta^2\text{-H}_3\text{SiC}_2\text{SiH}_3)$ for $\text{M} = \text{Ti}$ on the basis of B3LYP density functional theory. The interactions of metals Zr and Hf with alkynes in such complexes have also been calculated. The results of the calculated structural parameters were in excellent agreement with available X-ray molecular structural data. The conclusion of this was the description that the alkyne complexes prefer the metallacyclopropene resonance structure with two in-plane $\text{M}-\text{C}$ σ -bonds and one out-of-plane π -bond interacting with the metal center. This gives a delocalized three center and two-electron system. After the bonding analysis and the computed stabilization interaction, these alkyne complexes were characterized as aromatic on the basis of the computed nucleus-independent chemical shifts (NICS) at the center of the 3-membered rings over the center of the 3-membered rings.

Very recently, further calculations of such compounds were presented in a paper by Aysin, Leites and Bukalov for a better general understanding of the bonding in 1-heterocyclopropenes regarding the “Aromaticity of 1 Heterocyclopropenes Containing an Atom of Group 14 or 4”.^[3] In addition to the earlier published results of calculations from the authors for the group 4 metallocene alkyne complexes, structural, electronic (FBO), optical (vibrational spectroscopy), energetic (ISE), and magnetic (NICS scan, GIMIC) criteria for aromaticity were discussed. The obtained results characterize the hetero-cyclopropenes of Si and Ge with aromatic properties as σ^* or pseudo- π , whereas all-C-cyclopropenes are σ -aromatic. The bond indices and the aromaticity descriptors ISE as well as the NICS scan show that the silacyclopropene is more aromatic than the germa-cyclopropene. In contrast to these results, the group 4 metallacyclopropenes $\text{Cp}_2\text{M}(\eta^2\text{-RC}_2\text{R})$ with $\text{M} = \text{Ti, Zr}$ and Hf are not aromatic according to the NICS scan, the GIMIC results and the analysis of the MO bonding scheme. This constitutes a fundamental difference between group 14 and group 4 heterocyclopropenes.

3. Substitution of $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ and Coordination of Substrates

The substitution of $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ for substrates like $\text{RE}=\text{ER}$ to give complexes of the type $\text{Cp}_2\text{Ti}(\eta^2\text{-RE}_2\text{R})$ and $\text{Cp}_2\text{Zr}(\text{L})(\eta^2\text{-RE}_2\text{R})$ of main group elements like N, P and Sb has already been described. In a series of investigations, starting from Cp_2Ti -

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(CO)₂^[4a] or Cp₂ZrCl₂ and Li₂[PhN₂Ph],^[4b] the complexes Cp₂M(L)(η²-PhN₂Ph) (M = Ti without L and M = Zr) were obtained, too. Reactions of (*rac*-ebthi)M(η²-Me₃SiC₂SiMe₃) (M = Ti, Zr, ebthi = ethylene-1,2-bis(5-4,5,6,7-tetrahydro-1-indenyl)), Cp^{*}₂Ti(η²-Me₃SiC₂SiMe₃), Cp₂Ti(η²-Me₃SiC₂SiMe₃) and Cp₂Zr(py)(η²-Me₃SiC₂SiMe₃) with PhN=NPh gave, after dissociation of Me₃SiC₂SiMe₃, different complexes of this type, sometimes together with other products.^[4c]

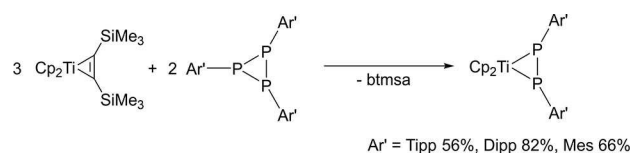
The selective conversion of aryl-substituted triphosphiranes (Ar₃P)₃ to titanocene diphosphene complexes Cp₂Ti(η²-Ar₂P₂Ar₂) was observed by Hering-Junghans and coworkers in the reaction with Cp₂Ti(η²-Me₃SiC₂SiMe₃) (Scheme 1). This was described for Ar' = Tipp = 2,4,6-*i*Pr₃C₆H₂; Dipp = 2,6-*i*Pr₃C₆H₂; Mes = 2,4,6-Me₃C₆H₂.^[4d]

Some time ago, Breunig and coworkers obtained the complex Cp₂Ti(η²-2,6-Me₃C₆H₃-Sb₂-2,6-Me₃C₆H₃) by the reaction of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with 2,6-Me₃C₆H₃SbH₂.^[4e] Very recently, Hering-Junghans and coworkers extended the series of such compounds and disclosed the analogous arsenic complexes Cp₂Ti(η²-Ar₂As₂Ar₂) with Ar' = Tipp, Dipp, Ter (Scheme 2; Ter = terphenyl).^[5a]

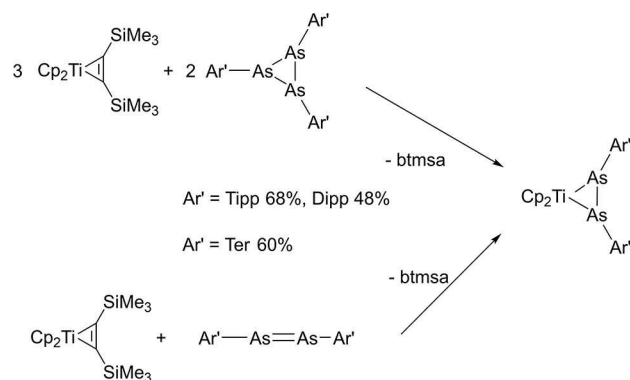
In the reaction of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with (Ar'-As)₃, the complexes Cp₂Ti(η²-Ar₂As₂Ar₂) with Ar' = Tipp, Dipp were formed (Scheme 2). The compound Ar'As=AsAr' with Ar' = Ter reacts with Cp₂Ti(η²-Me₃SiC₂SiMe₃) to form such a complex, too. In all these typical reactions, btmsa only acts as a spectator ligand, and by its dissociation, the highly coordinatively and electronically unsaturated reactive 14-electron [Cp₂Ti] fragment is formed.^[5a]

In a recently published excellent paper from Hering-Junghans, Reiß and coworkers, the reactions of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with phospho- and arsa-Wittig reagents to different products were described (Scheme 3).^[5b]

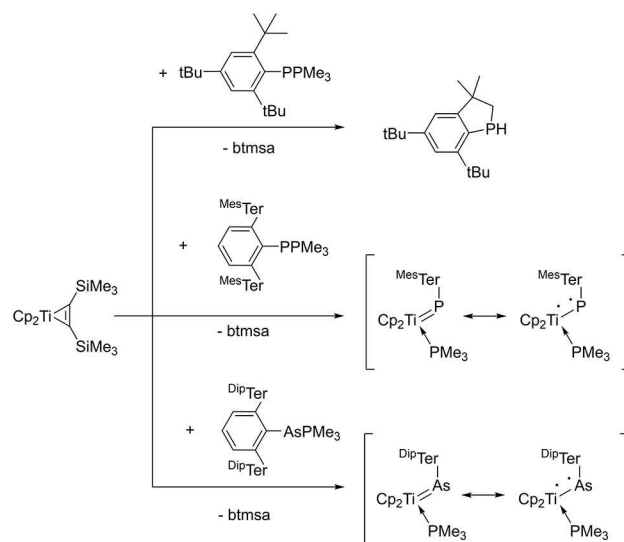
In the reaction with Mes*PPMe₃ (Mes* = 2,4,6-tri-*tert*-butylphenyl), the known 3,3-dimethyl-5,7-di-*tert*-butylphosphindane



Scheme 1. Formation of titanocene diphosphene complexes Cp₂Ti(η²-Ar₂P₂Ar₂).



Scheme 2. Reactions of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with (Ar'-As)₃ and Ar'As=As-Ar' to complexes Cp₂Ti(η²-Ar₂As₂Ar₂).



Scheme 3. Reaction products of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with phospho- and arsa-Wittig reagents like phosphindane and PMe₃-stabilized phosphinidene as well as arsinidene complexes.

was obtained. In the reaction with Mes*TerPPMe₃ (Mes*Ter = 2,6-Me₃C₆H₃, Mes = 2,4,6-Me₃C₆H₂) the PMe₃-stabilized titanocene phosphinidene complex Cp₂(PMe₃)Ti=P^{Mes}Ter was formed (Dip*Ter = 2,6-Dip₂C₆H₃). The reaction of Cp₂Ti(η²-Me₃SiC₂SiMe₃) with the potential arsa-Wittig reagent Dip*TerAsPMe₃ gave the analogous PMe₃-stabilized titanocene arsinidene complex Cp₂(PMe₃)Ti=As^{Dip}Ter. The latter was detected together with diarsene (Dip*TerAs)₂ if substoichiometric amounts of the starting titanium complex were used. The syntheses of the titanocene phosphinidene and arsinidene complexes with Ti=P and Ti=As



Uwe Rosenhal studied chemistry (1968-72), received his Ph.D. under the supervision of E. Kurras (1976), and completed his habilitation (1991) at the University of Rostock. After postdoctoral time at the A. N. Nesmeyanov Institute of Organoelement Compounds (IN-EOS) at the Russian Academy of Sciences in Moscow with M. E. Vol'pin and V. B. Shur (1988) he was a visiting research scientist at the Max Planck Institute of Kohlenforschung in Mülheim/Ruhr with G. Wilke and K. Pörschke (1990-91). He headed (1992-96) the Max Planck Research group "Complex Catalysis" and became Professor of Inorganic Chemistry at the University of Rostock (1993). As Deputy Director of the Leibniz Institute of Catalysis at the University of Rostock (2003-16), his scientific interests are up to now the basics of Organometallic Chemistry (unusual metallacycles) for applications in Homogeneous Catalysis (effective tri- and tetramerization of alkynes, selective oligomerization of ethylene).

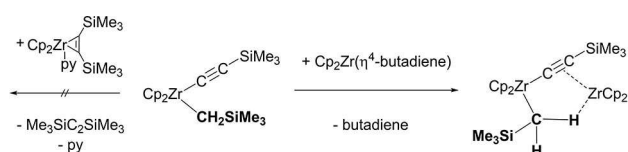
double bonds was realized, which are best described as singlet biradicaloids (Scheme 3).

Beweries, Reiß and coworkers reported on "Mechanistic Insights into Dehydrocoupling of Amine Boranes using Dinuclear Zirconocene Complexes".^[6] In these studies, they were interested in modelling some single reaction steps for the dehydrocoupling and used the complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ which, after dissociation of the alkyne and pyridine, serves as a generator for $[\text{Cp}_2\text{Zr}]$. Reacting $\text{Cp}_2\text{Zr}(\text{-CH}_2\text{SiMe}_3)(\text{-C}\equiv\text{CSiMe}_3)$ with $\text{Cp}_2\text{Zr}(\eta^4\text{-butadiene})$, they obtained a dinuclear hydride-bridged zirconocene complex (Scheme 4). This reaction was not possible when using the alkyne complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ instead.

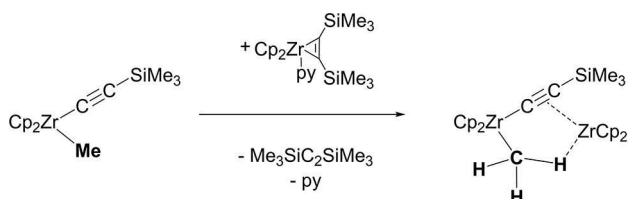
If the structurally similar $\text{Cp}_2\text{Zr}(\text{-Me})(\text{-C}\equiv\text{CSiMe}_3)$ was employed instead of $\text{Cp}_2\text{Zr}(\text{-CH}_2\text{SiMe}_3)(\text{-C}\equiv\text{CSiMe}_3)$, the reaction with $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ allowed the preparation of the corresponding dinuclear hydride-bridged zirconocene complex (Scheme 5).

4. Substitution of $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ by Substrates, Coupling Reactions and Investigations of the Obtained New Products

In the past, Staubitz and coworkers published a series of highly interesting papers in which the zirconocene complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ was used to synthesize tin-containing conjugated heterocycles.^[7] By intermolecular coupling reactions, several bis(thiophenyl)-substituted octadiynes were converted into zirconacyclopentadienes. During this very effective reaction, functional substituents like iodide stayed intact and the obtained zirconacyclopentadienes reacted by transmetalation to the respective stannole compounds. An interesting example was the reaction of thiophene-substituted stannoles which could be converted to polymers by Stille cross-coupling reactions.^[7a] Using the same method, several other stannoles



Scheme 4. Unsuccessful attempt of using $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ to obtain the dinuclear hydride-bridged zirconocene complex from $\text{Cp}_2\text{Zr}(\text{-CH}_2\text{SiMe}_3)(\text{-C}\equiv\text{CSiMe}_3)$.



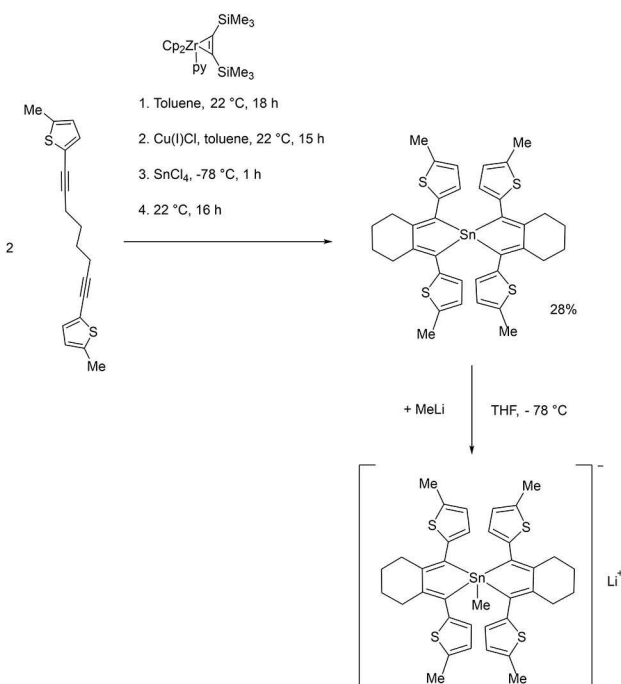
Scheme 5. Successful use of $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ to obtain the dinuclear hydride-bridged zirconocene complex from $\text{Cp}_2\text{Zr}(\text{-Me})(\text{-C}\equiv\text{CSiMe}_3)$.

were obtained.^[7b] During these investigations, it was shown, that the complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-btmsa})$ reacted faster and gave higher yields compared to the Negishi reagent. Additionally, functional groups were tolerated by this method, which was applied for several disubstituted alkynes and octadiynes to synthesize the corresponding zirconacyclopentadienes by internal coupling. Under transmetalation conditions with $\text{Ar}'_2\text{SnCl}_2$ ($\text{Ar}' = \text{-C}_6\text{F}_5, \text{-C}_6\text{H}_4\text{-p-OMe}, \text{-C}_6\text{H}_5$), several stannoles were obtained.^[7c,d]

In several new papers from the Staubitz group, the series of these very interesting investigations was extended to further syntheses.^[8] Experimental and theoretical studies of a spirostannole and the formation of a pentaorganostannate were reported (Scheme 6).^[8a] The new spirostannole 1,1',3,3'-tetrakis(5-methylthiophen-2-yl)-4,4',5,5',6,6',7,7'-octahydro-2,2'-spiro[benzo-c]stannole was synthesized, following the same procedure of coupling reaction of diynes with $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and subsequent transmetalation. The results of the geometry optimization by DFT calculations confirm the high planarity, leading to efficient conjugation within the molecule.

The obtained spirostannole was characterized as a strongly absorbing material, but an extremely weak emitter in solution. The emission only becomes visible when the solution is cooled. The molecular structure and the electronic behavior of the thermally unstable lithium pentaorganostannate was supported by DFT and TD-DFT calculations.

In another recent paper from the same group, the synthesis of four well-defined conjugated polymers, containing stannole units as unusual heterocyclic units in the main chain, was reported.^[8b] The stannole-thiophenyl copolymers were pro-

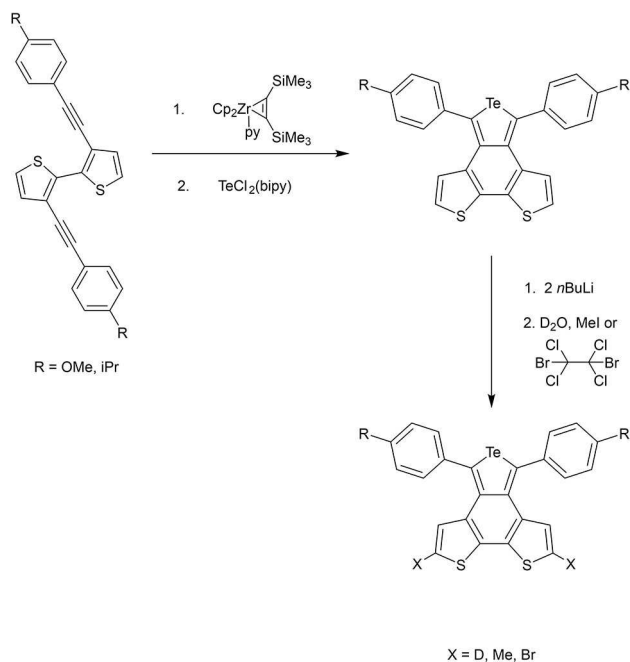


Scheme 6. Formation of a spirostannole by using $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and subsequent transmetalation and reaction to a pentaorganostannate.

duced by tin-selective Stille coupling reactions in nearly quantitative yields. NMR spectroscopic investigations suggested unaffected tin atoms in the rings. The optoelectronic properties of the iodothiophenyl-stannole monomers and the resulting bithiophenyl-stannole copolymers were investigated. The molecular structures of several stannoles were studied by single crystal X-ray analysis. Additionally, the influence of the replacement of thiophenes by stannoles in terthiophene and sexithiophene on their optoelectronic and electrochemical properties was investigated.^[8c] Generally, polystannoles with thienyl comonomers are similar to polythiophenes. By using well-defined oligothiophenes as a model to understand the optical and electrical properties of polythiophenes, the team tackled the question of the precise influence of thiophene units in a conjugated backbone of a polymer. These insights were followingly transferred to stannole-containing copolymers. Despite several differences, these materials exhibited a similar behavior to oligothiophenes. Recently, Staubitz and coworkers published a review concerning different methods for the synthesis of stannoles, in which such ring-fused and heteroatom-containing compounds were summarized.^[8d]

Rivard and coworkers had previously synthesized phosphorescent π -extended heteroarenes.^[9] The reaction of 5,6-dihydro-11,12-dihydrodibenz[a,e]cyclooctyne with $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ yielded zirconacyclopentadienes, which, with $(\text{bipy})\text{TeCl}_2$, were converted to "substituent-locked tellurophenes". More recently, Rivard and coworkers published a paper in which the complex $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ was used to synthesize tellura(benzo)bithiophenes (Scheme 7).^[10]

Several planar π -extended tellura(benzo)bithiophenes were synthesized with a tellurophene ring fused to a benzobisthiophene



Scheme 7. Reaction of 5,6-dihydro-11,12-dihydrodibenz[a,e]cyclooctyne with $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ to zirconacyclopentadienes and subsequent conversion with $(\text{bipy})\text{TeCl}_2$ to tellurophenes.

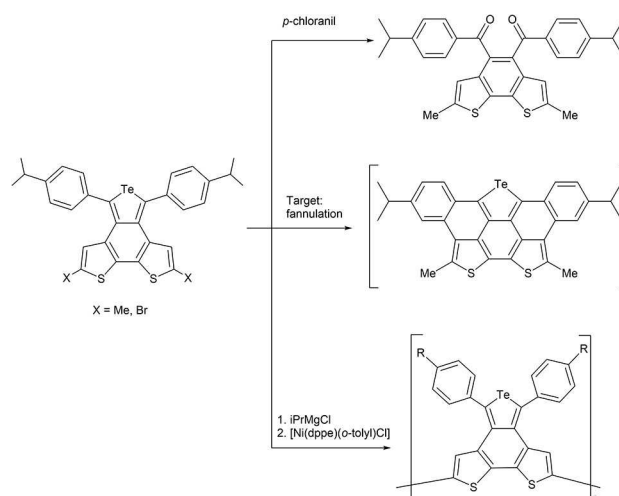
phene. In the 2- and 5-positions of the tellurophenes, aromatic substituents like $-\text{C}_6\text{H}_4\text{iPr}$ or $-\text{C}_6\text{H}_4\text{OCH}_3$ are located. The reaction of cumenyl ($-\text{C}_6\text{H}_4\text{iPr}$)-substituted tellura(benzo)-bis(thiophene) with *p*-chloranil led, by oxidation, to Te–C bond cleavage and the formation of an ene-dione (Scheme 8, top). An intramolecular annulation reaction to fuse the tellurophene rings to the aryl groups was only successfully calculated, but not experimentally realized (Scheme 8, center). The bromine-substituted compound reacted with $i\text{PrMgCl}$ and $[\text{Ni}(\text{dppe})(o\text{-tolyl})\text{Cl}]$, via the metalated tellural(benzo)bithiophene, to a polymer. The data of the obtained products indicated electronic and structural features for phosphorescence in this compound class.

In a series of very interesting papers, Tilley and coworkers had reported the use of $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ for site-selective $[2+2+n]$ cycloadditions.^[11] The rapid, scalable access to PAHs (polycyclic aromatic hydrocarbons) with alkynyl groups was reported in detail for many examples. In one of these papers, the $[2+2+1]$ addition reaction by $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with a subsequent transmetalation for the synthesis of alkynylated selenophene-annulated PAHs was described.^[11e]

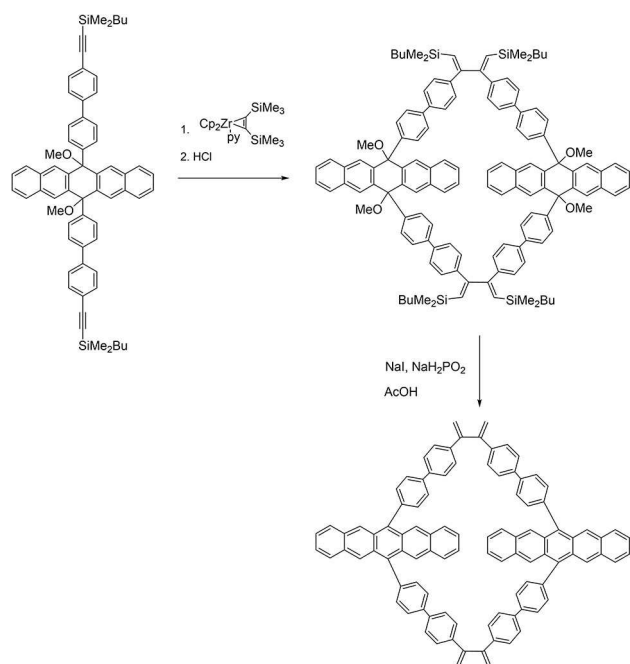
In a recent paper by Tilley et al., a special zirconocene-mediated cyclic coupling reaction of compounds with two alkynyl groups was published (Schemes 9 and 10).^[12a] In some cases, the zirconocene-catalyzed macrocyclization is reversible through a dynamic C–C bond formation, which was investigated and calculated in detail.^[12] Additionally, the different obtained products were investigated regarding their X-ray molecular structures and photophysical properties.

The formation of the macrocycles was observed either as a nonselective or as a selective di- or trimerization to yield two geometrically distinct pentacene-containing macrocycles.

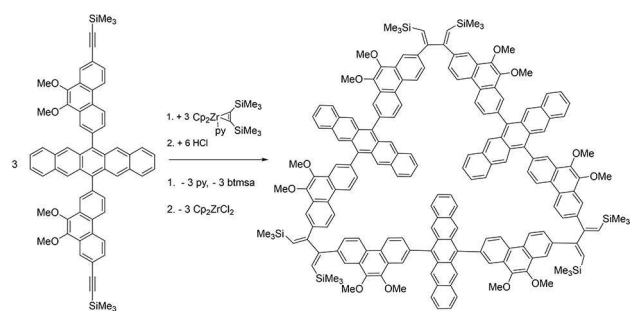
For a general understanding of these reactions, Tilley and Miller discussed ligand effects on such zirconacyclopentadiene formations and their reversibility.^[12b] Zirconacyclopentadienes are important intermediates for the synthesis of (*E,E*)-buta-



Scheme 8. Oxidative cleavage of Te–C bonds to yield an ene-dione; attempted intramolecular annulation; and preparation of a polymer.



Scheme 9. Selective dimerization by $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)_2$ yielding a macrocycle.



Scheme 10. Selective trimerization to a macrocycle by using $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)_2$

dienes, substituted benzenes, thiophenes and conjugated polymers as well as for macrocycles. For this reason, cycloreversion reactions are important for the selective syntheses of these complexes. The authors presented a systematic study of the influence of Cp substituents on the zirconocene coupling reaction of alkynes. Zirconocenes with two cyclopentadienyl (Cp/Cp) and a combination of pentamethylcyclopentadiene/nonsubstituted cyclopentadiene (Cp/Cp*) as well as the *ansa*-bridged $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2]$ units were compared. The reversible alkyne coupling of zirconacyclopentadienes with SiMe_3 substituents was studied, and the rates of decoupling under the influence of PMe_3 were measured. The use of different Cp ligands at zirconium has a significant effect on the rates of the reversibility of alkyne coupling reactions. This is important to get useful information to understand and to optimize the selective coupling to macrocycles and oligomers.

Very recently, Tilley and co-workers reported a new synthetic strategy for the synthesis of new carbon nanobelts

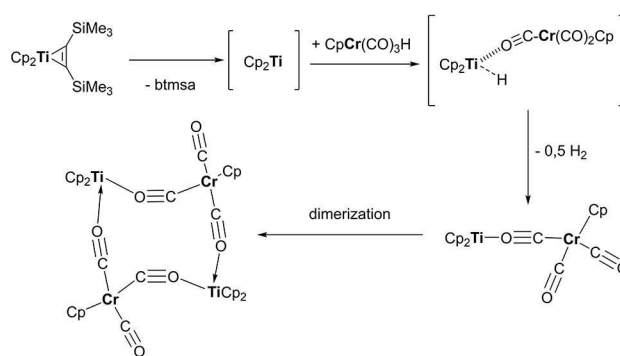
(CNBs). Starting from highly fused monomers and using a site-selective $[2+2+2]$ cycloaddition with $\text{Cp}_2(\text{py})\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$, a high-yielding macrocyclization was realized on large scale.^[12c] The authors concluded that this synthetic method constitutes a general principle for greater synthetic efficiency. The highly fused monomeric building blocks have significant advantages, reducing problems associated with the introduction of strain into the fused-ring macrocycles. The method is described as an important step in the formation of technologically valuable building blocks for more complex materials.

It might be worth mentioning that the authors concluded that the robust synthetic strategies for the synthesis of these two unique pentacene-containing macrocycles were only possible by using the zirconocene coupling strategy.

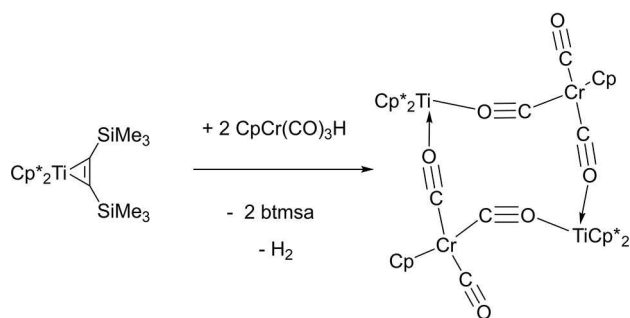
Norton and coworkers published reactions of the titanium bis(trimethylsilyl)acetylene complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with $\text{CpCr}(\text{CO})_3\text{H}$ (Scheme 11).^[13a] As mentioned before, in these complexes the alkyne dissociates and thus the reactivities of titanocene complexes $[\text{Cp}_2\text{Ti}]$ and $[\text{Cp}^*\text{Ti}]$ were studied. With $\text{CpCr}(\text{CO})_3\text{H}$, an addition to form $\text{Ti}^{\text{IV}}\text{-H}$ intermediates followed by loss of H_2 under formation of bimetallic $\text{Ti}^{\text{III}}\text{-Cr}$ complexes was described.

The formed complexes show a dimeric geometry with a 12-membered Ti_2Cr_2 ring with bridging CO ligands and Ti-O-Cr units. The terminal carbonyls are *trans*-coordinated to each other. According to DFT calculations, the processes for loss of H_2 from the $\text{Ti}^{\text{IV}}\text{-H}$ intermediates and the formation of the $\text{Ti}^{\text{III}}\text{-Cr}$ dimer are exergonic. It is somewhat surprising that there was no coupling of CO, as had been observed, for example, by Berry and Bercaw for a bimetallic Zr-Fe complex^[13b] or as it was discussed for other reactions of CO.^[13c,d] The same reaction type was described for $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{CpCr}(\text{CO})_3\text{H}$ (Scheme 12).

In comparison to the above-described reactions of the complexes $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with $\text{Cp}'=\text{Cp}$, Cp^* and $\text{CpCr}(\text{CO})_3\text{H}$, complex $\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2)\text{Ti}(\text{-CH}_3)$ reacts with $\text{CpCr}(\text{CO})_3\text{H}$ to yield a $\text{Ti}^{\text{IV}}\text{-CH}_3$ species with a coordinated $\text{CpCr}(\text{CO})_3$ anion.



Scheme 11. Mechanism for the reaction of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with $\text{CpCr}(\text{CO})_3\text{H}$.

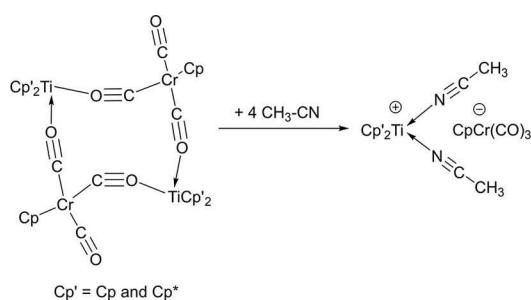


Scheme 12. Reaction of $\text{Cp}^*_2\text{Ti}(\eta^1\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with $\text{CpCr}(\text{CO})_3\text{H}$.

5. Reactions of the Formed New Coordination Compounds

Upon coordination of solvents like CH_3CN , the observed solvatochromic shifts of the two tetranuclear Ti_2Cr_2 compounds indicate the breakdown of the dimeric structures (Scheme 13).^[13a]

The above-mentioned 12-membered heterobimetallic $\text{Ti}^{\text{III}}\text{-Cr}$ complexes showed activity as catalysts for the hydrogenation of an epoxide to yield an anti-Markovnikov alcohol (Scheme 14).^[13a] This was possible without the use of Cp_2TiX_2 ($\text{X} = \text{Cl}$, mesylate), $\text{NaCpCr}(\text{CO})_3$, and $\text{HCpCr}(\text{CO})_3$ as described in previous catalytic systems from the authors.



Scheme 13. Coordination of CH_3CN to the tetranuclear Ti_2Cr_2 -ring compounds.



Scheme 14. Catalytic hydrogenation of an epoxide to an anti-Markovnikov alcohol using the Ti_2Cr_2 ring compound as catalyst.

6. Recently Published Reviews with Remarks for Reactions of Group 4 Bis(trimethylsilyl)acetylene Metallocene Complexes

In several recently published reviews, group 4 bis(trimethylsilyl)acetylene metallocene complexes were mentioned or discussed in detail in the context of their special reactivity.

Tonks and coworkers summarized published examples for multicomponent syntheses of 5- and 6-membered aromatic heterocycles by group 4–8 transition metal catalysts.^[14a] They mentioned tetrasubstituted pyrazines as the products of nitriles, magnesium and Cp_2TiCl_2 . For these reactions, 2,5-diazatitanacyclopentadienes were assumed as intermediates which were formed from $\text{Cp}_2\text{Ti}(\eta^1\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ after alkyne dissociation and tail-to-tail coupling of two nitrile molecules at Cp_2Ti .^[14b,c] These metallacycles then formed tetrasubstituted several pyrazines through transmetalation from Ti to Al.^[14d] For pyrazine formation, a ring expansion by two further nitrile insertions into the diazatitanacyclopentadienes to 1,3,6,8-tetraaza-titanacyclononotetraenes was assumed. With EtAlCl_2 , these compounds would, after transmetalation, yield the Et-substituted 1,3,6,8-tetraazaaluminum-cyclononotetraenes together with Cp_2TiCl_2 . After hydrolysis, tetrasubstituted pyrazines were obtained in good yields.

In another review, Tamm and coworkers described and compared results of the syntheses and coordination chemistry of heteroatom-substituted alkynes for the example of diaminoacetylenes.^[14e] They mentioned previous results of reactions of dipiperidinoacetylene with titanocene and zirconocene $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ complexes.^[14f] With metallocenes $[\text{Cp}'_2\text{M}]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$), metallacyclopentadienes were formed, whereas the sterically more demanding decamethylmetallocenes $[\text{Cp}^*_2\text{M}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) gave metallacyclopropenes. Group 4 complexes of the heteroatom-substituted alkynes, such as diaminoacetylenes $\text{R}_2\text{NC}_2\text{NR}_2$, were compared to $\text{Me}_3\text{SiC}_2\text{SiMe}_3$ complexes. Some of these complexes were synthesized by reduction of $\text{Cp}'_2\text{MCl}_2$ ($\text{Cp}' = \eta^5\text{-Cp}$ and $\eta^5\text{-Cp}^*$) with magnesium in the presence of the diaminoacetylenes. According to NMR spectroscopic studies in solution, the zirconium complexes exist in an equilibrium with the tucked-in tetramethylpentafulvene-diaminovinyl isomer. The latter is formed by an intramolecular CH bond activation and hydrogen transfer.

In a very recent review, Tonks reported details of the progress in Ti-catalyzed and -mediated oxidative amination reactions which formally proceed through $\text{Ti}^{\text{II}}/\text{Ti}^{\text{IV}}$ catalytic cycles.^[14g] He mentioned an older paper about the preparation and regioselective reactions of the zirconocene alkyne complex without stabilizing phosphane ligands $\text{Cp}_2\text{Zr}(\text{THF})(\eta^1\text{-tBuC}_2\text{SiMe}_3)$.^[14h] He further summarized and discussed the regiocontrol of the coupling reactions of Me_3Si -substituted alkynes, RC_2SiMe_3 , with the partner alkyne. This is strongly influenced by the different alkyne substituents, because the $\text{Ti}-\text{CSiMe}_3$ bond is stronger than the $\text{Ti}-\text{CR}$ bond. This was analyzed for other insertion reactions of group 4 metallocenes and used to control regioselectivity in reductive coupling

reactions. The above-mentioned regioselective reactions of $\text{Cp}_2\text{Zr}(\text{THF})(\eta^2\text{-tBuC}_2\text{SiMe}_3)$ are not directly connected to the here considered titanocene and zirconocene bis(trimethylsilyl)acetylene complexes, but provide insight how, by simple modification of the alkyne substituents, one can modify the coupling selectivity. In principle, this is important for the mentioned coupling reactions of Staubitz^[7,8] and Tilley.^[11,12] These considerations are also useful regarding the selective syntheses of zirconacyclopentadiene intermediates, which are important for the subsequent clean synthesis of (*E,E*)-butadienes, transmetalation products, macrocycles and others.^[14g]

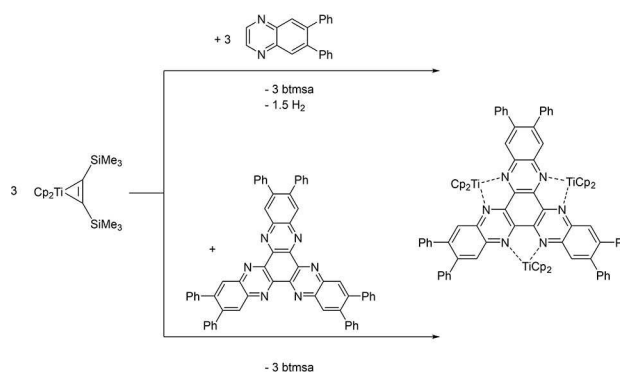
Very recently, Fortin and Gomez-Torres described the redox chemistry of low-valent titanium complexes and low-valent titanium synthons.^[14i] They mentioned, among other examples, the previously published reactions of $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{Cp}' = \text{Cp}$ and Cp^*) with water, methanol, phenol, and thiophenol, yielding $(\text{Cp}_2\text{Ti})_2(\mu\text{-O})$, $\text{Cp}^*\text{Ti}(\text{OH})_2$, $(\text{Cp}_2\text{Ti})_2(\mu\text{-OMe})_2$, $\text{Cp}^*\text{Ti}(\text{H})(\text{OMe})$, $\text{Cp}'_2\text{Ti}(\text{OC}_6\text{H}_4\text{Me})_2$, and $\text{Cp}'_2\text{Ti}(\text{SPh})_2$, respectively. In addition to this protonation chemistry of $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$, other examples for the formation of divalent titanocene sources $[\text{Cp}'_2\text{Ti}]$ as LVT (low-valent titanium) synthons were summarized. The reactions of $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with I_2 forms trivalent $(\text{Cp}'_2\text{Ti})_2(\mu\text{-I})_2$ and tetravalent complexes $\text{Cp}'_2\text{Ti}_2$.

$\text{Cp}'_2\text{Ti}(\text{Me})$ species were formed by the oxidative addition of the Me-I bond. The 2,2'-bipyridine radical monoanion $\text{Cp}^*\text{Ti}(\text{bipy})$, was obtained by the reduction of 2,2'-bipyridine by $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$. With 4,5-diazofluorene, 0.5 equiv. of H_2 are formed together with an N,N'-bound diazafluorenyl complex. Beckhaus and coworkers extended the chemistry of the $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ complexes to multinuclear complexes,^[15] like $[(\text{Cp}_2\text{Ti})_3\text{-HATN}(\text{Ph})_6]$ ($\text{HATN}(\text{Ph})_6 = \text{hexaphenyl-5,6,11,12,17,18-hexaazatrinaphthylene}$) with multi-electron transfers in the extended π -systems (see below).^[16] Titanium complexes with multiple titanium–ligand bonds were obtained by the reaction of *m*-terphenyl azide with $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ to yield terminal imido complexes.

7. Investigations of Former Obtained Products

As mentioned above, Beckhaus and coworkers obtained the trinuclear hexaphenyl-5,6,11,12,17,18-hexaazatrinaphthylene-tris-titanocene $(\text{Cp}_2\text{Ti})_3(\mu^3\text{-HATNPh}_6)$ either through dehydrogenative coupling of 6,7-diphenylquinoxaline in the presence of $\text{Cp}_2\text{Ti}(\eta^2\text{-btmsa})$ or through direct coordination of this fragment to the preformed HATNPh_6 ligand (Scheme 15).^[15]

In recent paper by Klüner, Beckhaus, Wittstock and coworkers, the electronic transitions in different redox states of 5,6,11,12,17,18-hexaazatrinaphthylene-bridged complexes were investigated regarding their spectroelectrochemical properties and their quantum chemistry.^[16] Such multinuclear transition metal complexes, bridged by ligands with extended π -electronic systems, show a variety of complex electronic transitions. While photochemistry and electrochemistry for binuclear complexes was described on several occasions, the related trinuclear complexes are less studied. Hexaphenyl-5,6,11,12,17,18-hexa-

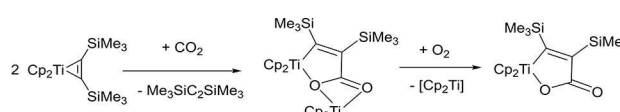


Scheme 15. Different formation of $(\text{Cp}_2\text{Ti})_3(\mu^3\text{-HATNPh}_6)$ from $\text{Cp}_2\text{Ti}(\eta^2\text{-btmsa})$.

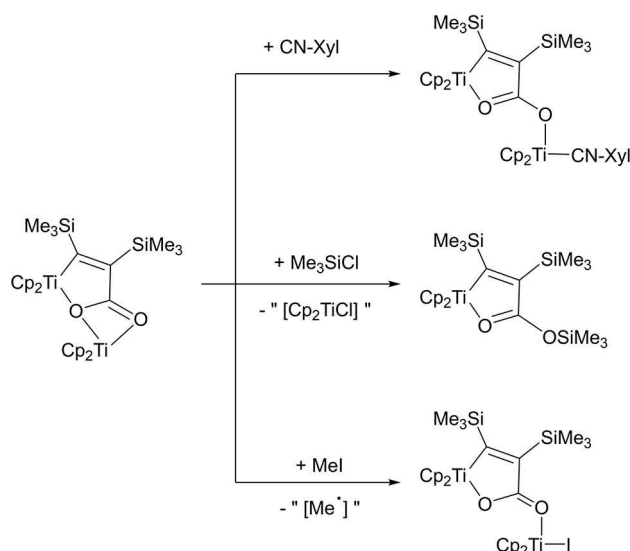
azatrinaphthylene-tris-titanocene $(\text{Cp}_2\text{Ti})_3\text{HATN}(\text{Ph})_6$ shows six oxidation and three reduction waves in the voltammogram. The spectra in solution and the electrochemically formed oxidation products showed electronic transitions in the UV, visible and the NIR ranges. The results of the DFT and linear response time-dependent DFT calculations point at three formally titanium(II) centers with a transfer of an electron to the HATN ligand in the ground state. The optically excited transitions occur only between ligand-centered orbitals. The charged titanium centers provide an electrostatic frame to the extended π -electronic system. The complete active self-consistent field (CASSCF) calculation on a simplified model compound considered the multi-reference character of the three titanium centers. The interpretation of the experimentally observed temperature-dependent magnetic behavior of the different redox states of this compound corresponds to self-assembly reactions of multinuclear complexes mediated by group 4 metallocenes.

Some time ago, coupling reactions of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with carbon dioxide were investigated.^[17] With $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$, a dinuclear vinylcarboxylate complex was formed which, upon reaction with oxygen, gave a titanafuranone (Scheme 16).

Reactivity and electronic structure analysis of such bimetallic bis-titanocene vinylcarboxylate complexes was published in a very recent paper by Powers, Tonks and coworkers (Scheme 17).^[18] They reported three new reactions of the dinuclear $\text{Ti}^{\text{II}}/\text{Ti}^{\text{III}}$ complex $[(\text{Cp}_2\text{Ti})_2\{\text{O}_2\text{C}_3(\text{Me}_3\text{Si})_2\}]$, characterizing a different reactivity pattern of the reduced dititanium centers. The electronic structure of the obtained compounds was studied by X-ray diffraction and EPR analyses. These electronic structures were used for the covalent bond classification and the electron counting method. Starting from $[(\text{Cp}_2\text{Ti})_2\{\text{O}_2\text{C}_3(\text{Me}_3\text{Si})_2\}]$, the coordination of CNXyl ($\text{Xyl} = 2,6\text{-}(\text{Me})_2\text{C}_6\text{H}_3$) resulted in formation of another bimetallic complex,



Scheme 16. Reactions of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with carbon dioxide.



Scheme 17. Reactions of the dinuclear vinylcarboxylate complex $[(\text{Cp}_2\text{Ti})_2(\text{O}_2\text{C}_3(\text{Me}_3\text{Si})_2)]$.

which after XRD, EPR, and IR analyses was described as a $\text{Ti}^{\text{II}}/\text{Ti}^{\text{III}}$ electronic structure. The products of reactions with electrophiles were found to depend on the character of the used electrophiles. The reaction with Me_3SiCl leads to a monometallic Ti^{III} complex with a chelating α,β -unsaturated silyl ester ligand. The complex was formed by formal substitution of $[\text{Cp}_2\text{Ti}]$ by the trimethylsilyl group. With methyl iodide, a radical reaction was observed, in which oxidation of one titanium to yield a mixed valent $\text{Ti}^{\text{III}}/\text{Ti}^{\text{IV}}$ complex was observed.

These results are in agreement with suggestions that in the bimetallic core a cooperative reactivity is possible through electronic communication. The authors mentioned that their studies about “*the fundamental oxidation chemistry of these complexes will hopefully motivate future work on catalytic reactions related to organometallic CO_2 coupling using Ti.*”

8. Actinide Metallocene Bis(trimethylsilyl)acetylene Complexes

Several publications in the past have shown that the typical alkyne substitution of group 4 metallocene bis(trimethylsilyl)acetylene complexes is possible with actinide metallocenes, too. This was published by Zi, Walter et al.^[19] as well as by Kiplinger and coworkers.^[20]

In addition to this, new investigations reemphasize the transfer of group 4 reactivity patterns to actinide metallocene complexes.^[21a] Zi, Walter and coworkers described the synthesis and reactivity of $\text{Cp}'_2\text{U}(\eta^2\text{-PhC}_2\text{Ph})$ with $\text{Cp}' = \eta^5\text{-1,2,4-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$.^[21a] This complex was compared to other uranium and thorium metallacyclopropenes. In the thorium metallacyclopropenes, the coordinated alkyne is inert toward ligand substitution and reacts with unsaturated molecules by inter- or intramolecular C–H bond activation. Like the uranium metal-

lacyclopropene complex $\text{Cp}^*\text{U}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$, $\text{Cp}'_2\text{U}(\eta^2\text{-PhC}_2\text{Ph})$ acts as a useful $[\text{Cp}'_2\text{U}^{\text{II}}]$ synthon for reactions with PhE_2Ph ($\text{E} = \text{S, Se}$) and unsaturated molecules like alkynes, imines, ketazines, bipy, nitriles, organic azides, and azo derivatives. The coordinated diphenylacetylene is replaced during the reaction, akin to the behavior of the group 4 metallocene bis(trimethylsilyl)acetylene complexes. The thorium and uranium metallacyclopropenes react in a similar way with isothiocyanates, aldehydes and ketones under insertion of the substrates yielding 5-membered heterometallacycles.

Zhang and coworkers very recently reported on reactions of metallacyclopropenes of lutetium and dysprosium toward nitriles which differ from the respective chemistry of scandacyclopropenes. New lanthanide metallacycles like azalutetacyclopentadienes, η^2 -pyrimidine dysprosium and a fused [5,6]lutetacycle as the first examples in rare-earth organometallic chemistry were obtained.^[21b] The insertion chemistry of lutetacyclopropene towards unsaturated CO and CN bonds was very recently published.^[21c] Again, these papers show some similarities for the typical alkyne substitution of group 4 metallocene bis(trimethylsilyl)acetylene complexes with similar and other actinide alkyne complexes.

9. Conclusion

During the last two years, reactions of the group 4 metallocene bis(trimethylsilyl)acetylene complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{py})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ were described. These complexes liberate bis(trimethylsilyl)acetylene and yield the very reactive low-valent titanium or zirconium center $[\text{Cp}'_2\text{M}]$ for $\text{M} = \text{Ti, Zr}$. As an extension of previously described examples, they react with several substrates to give coordination compounds, participate in coupling reactions and form heterobimetallic complexes. These new products were investigated in detail and have been used for new synthetic and catalytic reactions. Additionally, special applications for physicochemical purposes were found for some of these and previously obtained products. In addition to the summarized results of several reviews, the resulting preparative organometallic and organic chemistry has been described for recently published examples.

Notes

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: bis(trimethylsilyl)acetylene · group 4 transition metals · metallocenes · organometallic compounds · reactivity

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