What Do Titano- and Zirconocenes Do with Diynes and Polyynes?[‡]

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ABSTRACT

A thorough investigation of the reactions of diynes, $R(C{\equiv}C)_2R$, and polyynes, $R(C{\equiv}C)_nR$, with titanocene and zirconocene was performed using the metallocene sources $Cp_2M(L)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (M = Ti, L = –; M = Zr, L = THF, pyridine). The conversions show an array of different products generated in complexation, coupling, and cleavage reactions. These results include remarkable structures (e.g., five-membered metallacyclocumulenes) and reactions (e.g., C–C single-bond cleavage). In addition, the first C–C single-bond metathesis in homogeneous solution was discovered. The presented findings have been supported by theoretical studies.

Introduction

A suitable complex fragment that is both coordinatively and electronically unsaturated is required to realize a variety of stoichiometric and catalytic reactions of organometallic compounds with different substrates. Such a core complex coordinates to the chosen substrates, activates them, and moves them in the direction of the desired products. This general mechanism is nicely illustrated in manifold reactions of group 4 metallocenes. The complex fragments titanocene, "Cp_2Ti", and zirconocene, "Cp_2Zr", are unstable 14-electron compounds displaying a d^2 configuration (M(II)). They possess one lone-electron pair and two vacant valence orbitals, making their reactivity comparable to that of carbenes. The possible interactions between occupied and unoccupied orbitals explain why these metallocenes, "Cp_2M", react with a variety of unsaturated compounds to form metallacycles which then have the potential to undergo diverse conversions with further substrates. An important question in this context is what kind of ligand can be used that sufficiently stabilizes the metallocene fragment and that can be released quantitatively under mild conditions to generate the unstable and very reactive core complex. Possible answers to that problem were provided not only by an array of combined systems of Cp_2MX_2/reducing agent but also by some well-defined complexes Cp_2ML_n (e.g., M = Zr, L = *n*-butene, *n* = 1; M = Zr, L = 1,3-butadiene, *n* = 1; M = Ti, L = PMe_3, *n* = 2; etc.). These complexes are discussed in a number of reviews and various contributions in textbooks and are appreciated with regard to their importance in synthetic chemistry.[1] The applicability of these systems and their success in certain reactions often depend on their preparative accessibility, on the selectivity of the conversions, and on the inertness of the stand-in ligand. In recent years, we have successfully established alkyne complexes of the type $Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, L = –; M = Zr, L = THF, pyridine) as novel reagents for group 4 metallocene fragments. These react with a multitude of substrates, and in many cases the products explicitly differ from those obtained with conventional metallocene sources.[2] This can best be explained on the basis of the ready release of the silyl-substituted alkyne. For M = Zr, strong evidence has been found for an associative mechanism,[2c] while for M = Ti, the substitution can also run dissociatively via a free titanocene. The first examples of free titanocenes have very recently been published.[3]

Group 4 metallocenes play an important role in the stereospecific polymerization of olefins. For that reason, olefins have been the substrates of choice, and these were mainly studied in reactions with the metallocenes. In the range of a "modern acetylene chemistry",[4] which serves a variety of implementations (e.g., new materials, special polymers, nanostructures, supramolecular structures, etc.), substrates with C–C triple bonds have increasingly been investigated. After originally focusing on monoalkynes, researchers started to also concentrate on di-, oligo-, and polyynes. These substrates cause a greater complexity and

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Scheme 1

exo - exo

or

exo - endo

endo - endo
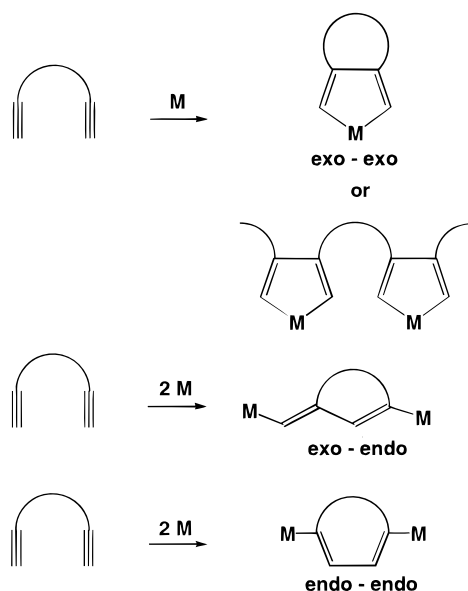
a decreased transparence of the reactions. But this drawback is compensated by the considerably greater attractiveness of the targeted structures which is due to the potential of spatial cross-linking.

The literature covers a large number of examples dealing with coupling and cyclization reactions involving low-valent titanium and zirconium compounds.[1] These reactions and those of diynes with other unsaturated substrates will not be covered in this paper. This Account exclusively considers products of the reactions of di-, oligo-, and polyynes with titano- and zirconocene. Emphasis is put on the conversions of 1,3-butadiynes with metallocenes which show remarkable, unusual structures (e.g., five-membered metallacyclocumulenes) and reactions (C−C single-bond cleavage and metathesis), while a decisive influence is exerted by the metals used, the diyne substituents, and the stoichiometry. These results illustrate again that the combination of transition metal compounds, substrates, and stoichiometry can lead to a fascinating and novel chemistry. The aim of this article is to give an overview of this exciting area of chemistry.

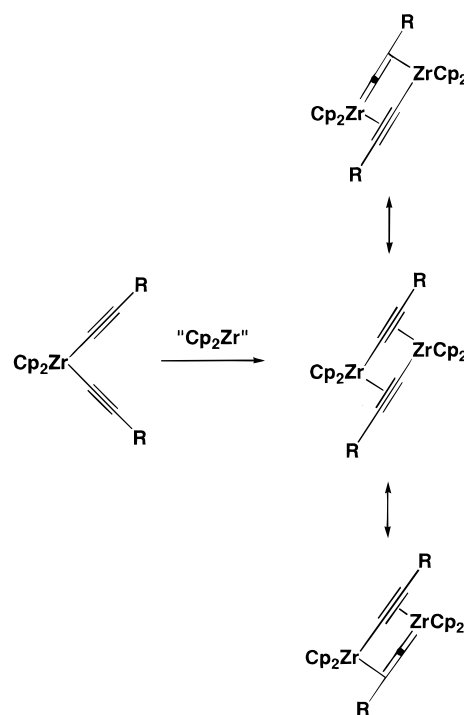So, what happens when titanocene and zirconocene react with these unsaturated moieties?

Nonconjugated Diynes and Triynes

The diversity of reactions of nonconjugated diynes $RC\equiv C-X-C\equiv CR$ with titanocene and zirconocene is very

Scheme 2

[Zr] = Zirconocenes
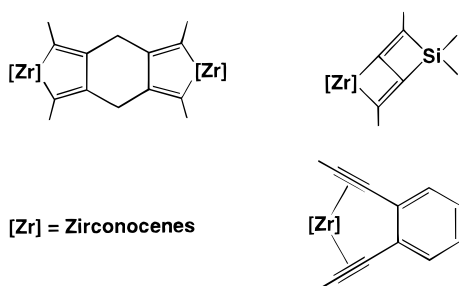
Scheme 3

extensive and therefore will be covered here just briefly. Principally, a differentiation between two possible reaction pathways can be made: we find coupling and complexation reactions. In the case of reductive cyclizations, the *exo−exo* coupling to afford metallacyclopentadienes is dominant (Scheme 1).

The coupling to mononuclear complexes has been found with a great variety of different bridges $X^{1,5}$ (e.g., M = Zr, X = $(CH_2)_2$, $(CH_2)_4$,[1b] M = Zr, X = CH_2OCH_2,[5a] PR,[5b] $B(NR_2)-CH_2-B(NR_2)$[5c]). Besides that, polymers, cyclotrimers, cyclotetramers, and macrocycles containing metallacyclopentadiene units could be synthesized, dependent on X^6 (e.g., M = Zr, X = p-$Me_2SiC_6H_4SiMe_2$,[6a] $Me_2SiC_6H_4-C_6H_4SiMe_2$,[6a] $C_6H_4C_6H_4$,[6b] bipyridyl[6c]).

Rather strikingly, the coupling for M = Zr and X = CH_2 leads to binuclear zirconacyclopentadiene complexes[7] (Scheme 2). Bis(alkynyl)silanes (X = SiR_2) afford annelated zirconacyclobutene−silacyclobutene compounds with Zr (Scheme 2),[8] whose formation can be rationalized by an initial coupling to zirconacyclopentadienes and a subsequent rearrangement. A 1:1 complexation results from R = $SiMe_3$ and X = o-C_6H_4. A coordination of the triple bond is observed for M = Zr, which does not lead to coupling (Scheme 2).[9] When organometallic diynes, e.g., X = Cp_2-Zr, are used, the reaction with zirconocene affords σ,π-acetylides (Scheme 3).[1h,27c] The nature of X seems to exert the decisive influence on which product is formed in these reactions.

The titanocene reagent $Cp_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$ (Figure 1) also forms mononuclear titanacyclopentadienes when it is reacted with nonconjugated diynes (X = $(CH_2)_n$, n = 2−6).

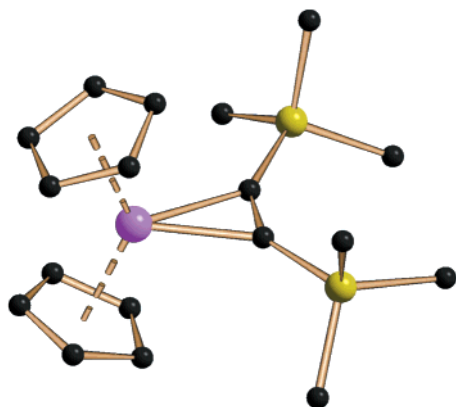In this context, it is of interest that the respective compound with n = 4 rearranges, via a Cp cleavage and

FIGURE 1. Molecular structure of Cp$_2$Ti(η^2-Me$_3$SiC$_2$SiMe$_3$).

an intramolecular C—C coupling, to a stable η^4,η^3-dihydroindenyltitanium complex.[10] The structural details of this compound reveal a strong (C—C)—Ti agostic, as seen by a comparison to very similar complexes (Scheme 4).[10,11]

The coupling of the nonconjugated triynes RSi(C$_6$H$_4$—C≡CSiMe$_3$)$_3$ at a zirconocene center lead, in a simple and effective way, to well-defined cage compounds.[12]
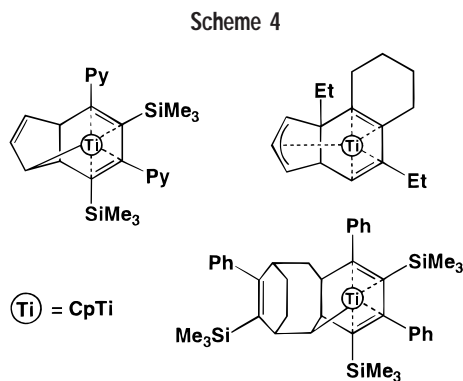
Reactions of 1,3-Butadiynes with Titanocene and Zirconocene

An overview of the products detected and fully characterized by the authors is presented in Scheme 5.

In the following, details concerning the modes of formation of these complexes will be discussed.
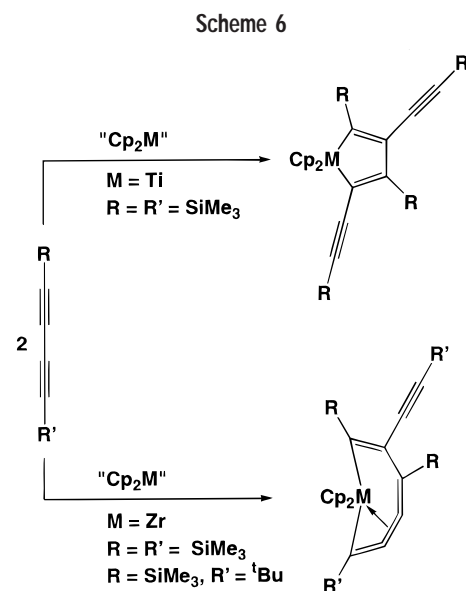
Coupling Reactions. The reaction of bis(trimethylsilyl)-butadiyne with zirconocene leads to a coupling product of two diyne entities at the core complex. The description of the formed product as a seven-membered zirconacyclocumulene (zirconacyclohepta-2,4,5,6-tetraene) follows from its determined X-ray structure (Scheme 6).[13]

Using analogous conditions with titanocene and employing 2 equiv of the diyne, a regioselective coupling of the diynes to a titanacyclopentadiene is observed, the product exhibiting one alkynyl group in the α- and another one in the β-position to the metal (Scheme 6).[14] It seems rather plausible that a five-membered ring is also formed for zirconium but that this zirconacyclopentadiyne then rearranges to the zirconacycloheptatetraene. This additional reaction step involving the alkynyl group in the α-position is obviously not feasible for the smaller titanium.

Scheme 4

(Ti) = CpTi

Scheme 5

Complexation

M = Ti, R = R = ^{t}Bu, Ph
R = SiMe$_3$, R' = ^{t}Bu, Ph

M = Ti, R = ^{t}Bu, Ph
M = Zr, R = ^{t}Bu

Cleavage

M = Ti, R = R' = SiMe$_3$
M = Zr, R = R' = SiMe$_3$
R = SiMe$_3$, R' = ^{t}Bu, Ph

Coupling

M = Ti, R = SiMe$_3$

M = Zr, R = R' = SiMe$_3$
R = SiMe$_3$, R' = ^{t}Bu
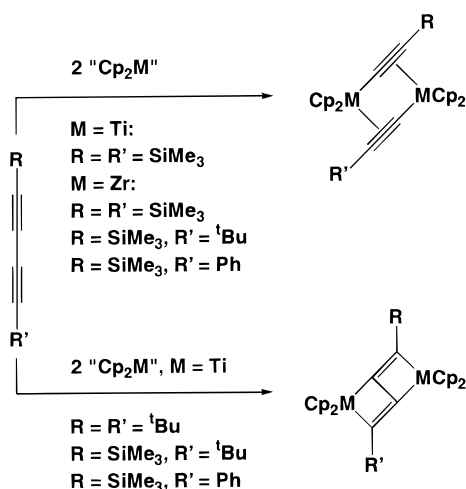
M = Ti, R = Ph

M = Ti, R = Ph
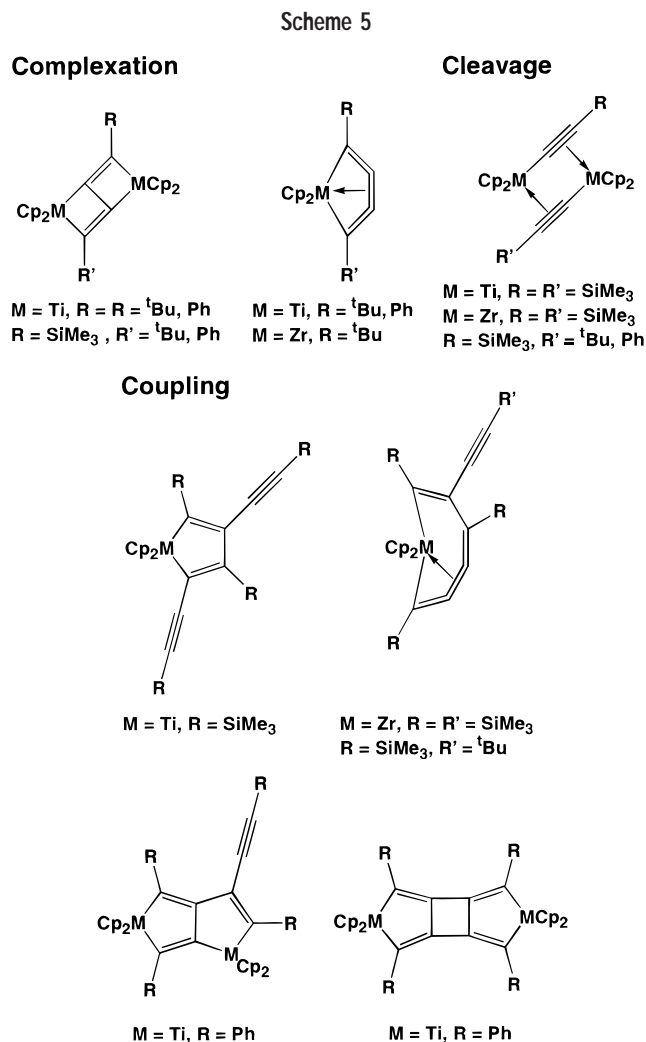
In addition to the described coupling of two diynes at a single metal center, there are examples of coupling reactions of two diynes between two metallocene fragments. These will be covered later in this text.

C—C Single-Bond Cleavage. Only changing the stoichiometry of the conversion can alter the reaction path-

Scheme 6

"Cp$_2$M"
M = Ti
R = R' = SiMe$_3$

"Cp$_2$M"
M = Zr
R = R' = SiMe$_3$
R = SiMe$_3$, R' = ^{t}Bu

Scheme 7

M = Ti:
R = R' = SiMe$_3$
M = Zr:
R = R' = SiMe$_3$
R = SiMe$_3$, R' = ^{t}Bu
R = SiMe$_3$, R' = Ph

R = R' = ^{t}Bu
R = SiMe$_3$, R' = ^{t}Bu
R = SiMe$_3$, R' = Ph

way, and the above-mentioned coupling reactions can be transformed to cleavage reactions if 2 equiv of the metallocene reacts with certain diynes (Scheme 7, upper part).[15]

The generated products are, from a formal point of view, twofold σ,π-alkynyl-bridged metal(III) complexes. These were previously known and thoroughly investigated, although they were always synthesized differently. A C—C single-bond activation in connection with a cleavage of that bond was a novel way to realize these compounds starting from 1,3-butadiynes. This type of cleavage reaction is favored for M = Zr[15b] as compared to Ti,[15a] an observation that is backed by theoretical calculations.[16] Additionally, there is a drastic influence of the substituents R attached to the butadiynes RC≡C—C≡CR, as exemplified by the trimethylsilyl group, which profoundly activates the inner C—C single bond by its β effect (withdrawing electron density at the C-β atoms). This explains why, for M = Ti, the bis(trimethylsilyl)butadiyne is the only diyne substrate which could have been cleaved so far.

Different Modes of Complexation. For M = Ti and diverse butadiynes, binuclear complexes with intact C$_4$ units between the two metal centers are formed under analogous conditions. The former diynes are transformed to "zigzag butadiyne ligands" or $\mu-\eta(1-3),\eta(2-4)$-*trans,trans*-tetradehydrobutadiene moieties between two metallocene cores (Scheme 7).[17] The first representative of this type of complex was obtained by Teuben and De Liefde Meijer in the reaction of [Cp$_2$TiCl]$_2$ with PhC≡CNa, which originally was assumed to be [Cp$_2$TiC≡CPh]$_2$.[17a] Later this complex was identified by Sekutowsky and Stucky as a dinuclear complex with a bridging butadiyne, as shown in the lower part of Scheme 7.[17b] So far, this
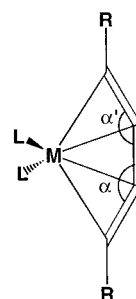
Scheme 8

"Cp$_2$M"

M = Ti, R = ^{t}Bu, Ph
M = Zr, R = ^{t}Bu
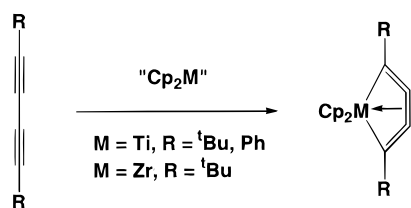
Scheme 9
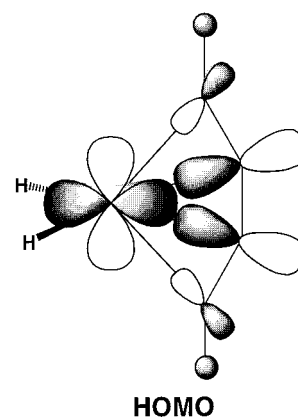
HOMO

M=Ti, L=Cl, R=H (calc.) [22]
(C=C): 1.311, 1.347, 1.311 Å
$\alpha = \alpha' = 142.4°$

M=Ti, L=Cp, R=^{t}Bu (exp.)[14]
(C=C) 1.243, 1.339, 1.276 Å
$\alpha = 150.0°, \alpha' = 147.8°$

M=Zr, L=Cl, R=H (calc.) [22]
(C=C): 1.324, 1.343, 1.324 Å
$\alpha = \alpha' = 144.8°$

M=Zr, L=Cp, R=^{t}Bu (exp.)[20]
(C=C) 1.28, 1.31, 1.29 Å
$\alpha = 150.0°, \alpha' = 147.2°$

bond type is not known for M = Zr, although theoretical calculations predict its existence in the case of certain substituents (e.g., CN).[18]

Besides this 2:1 complexation of the titanocene, a 1:1 complexation is observed when a different stoichiometry is employed. The butadiynes RC≡C—C≡CR with R = ^{t}Bu[14] and Ph[19] generate the novel five-membered titanacyclocumulenes (metallacyclopenta-2,3,4-trienes, η^4-1,2,3-butadiyne complexes) (Scheme 8). For R = ^{t}Bu, this structural type could also be realized with M = Zr.[20]

Scheme 10

Me$_2$CO

H$_2$O

Scheme 11
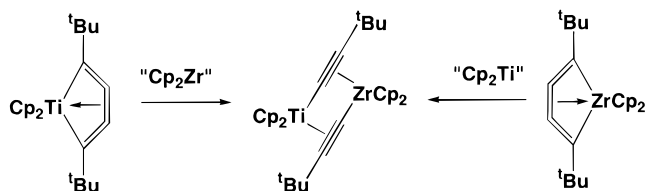

Scheme 13

L = PPh$_3$
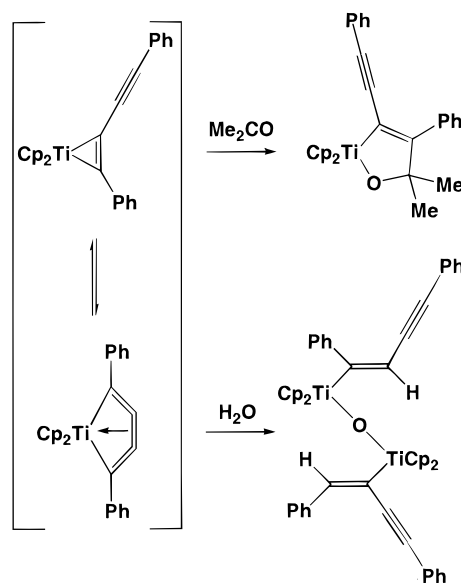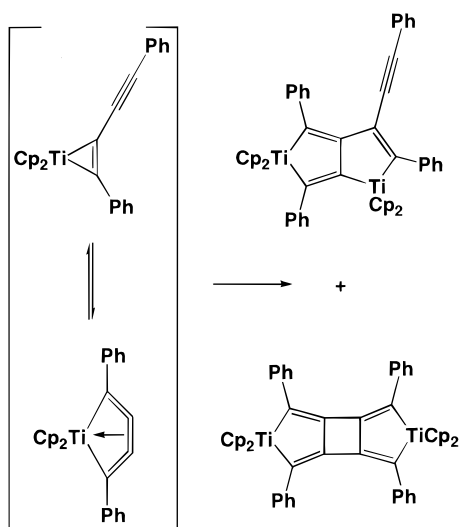
Structural and Theoretical Description of the Metallacyclocumulenes.

A five-membered metallacyclocumulene is very unusual. The structures of this type of compound display 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 to the metal center (Scheme 9).[14,20]

The distances and the angles (70−74° at C-α and 147−150° at C-β) in the metallacycle correspond closely to those of calculated organic cyclocumulenes such as cyclohexa- and cycloheptatrienes.[21] According to other theoretical calculations,[22] titana- and zirconacyclocumulenes are thermodynamically more stable than the isomeric bis(σ-acetylide) complexes. The calculated data are in good agreement with the obtained experimental values. All four carbon atoms of the former diyne are viewed to have 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 (Scheme 9).

Stoichiometric Reactions of the Metallacyclocumulenes.

Regarding some reactions of the metallacyclocumulenes, it is possible to assume an equilibrium between a η^4-complex (metallacyclocumulene) and a η^2-complex (metallacyclopropene).[19] For instance, the phenyl-substituted titanacyclocumulene reacts with acetone and water to yield insertion products that are typical for titanacyclopropenes (Scheme 10).[19]

Evidently, both forms of the equilibrium mixture react even with each other to afford an unsymmetric complex,
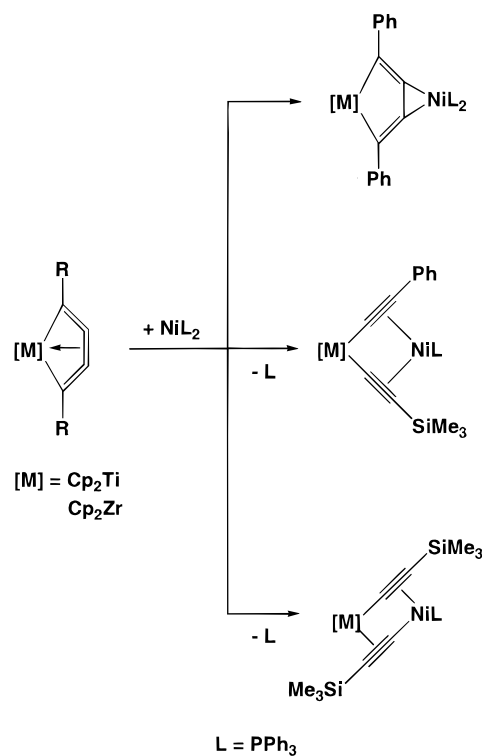
where a titanacyclopentadiene is annelated to a titanacyclopentene (Scheme 11).[19] This can be rationalized by an insertion of the internal double bond of the titanacyclocumulene into the titanacyclopropene.

Additionally, the symmetric titanium-substituted radialene is generated in the same solution. This can be thought of as a formal dimerization of two titanacyclocumulene molecules (Scheme 11).[18,23] If the titanacyclocumulene is treated with zirconocene or, the other way around, the zirconacyclocumulene with titanocene, identical Ti−Zr bimetallic complexes with two σ,π-alkynyl bridges are afforded (Scheme 12).[14]

The conversions with nickel(0) complexes prove a pointed dependence on the substituents R. For M = Ti and Zr and R = Ph, π-complexes of the corresponding metallacyclocumulenes are formed. They can be regarded as Ni(0)−olefin complexes (Scheme 13)[24] and are significant for two reasons.

On one hand, the homobimetallic analogues of these compounds can be viewed as the intermediates for the consecutive reaction to form the two different 2:1 complexes (cleavage and complexation reaction) (Scheme 7). On the other hand, they are a real complex-chemical proof for the metallacyclocumulene structure of the η^4-complex.[24,25] Meanwhile, such π-complexes of other metals with different metallacyclocumulenes are known.[26]

Scheme 12
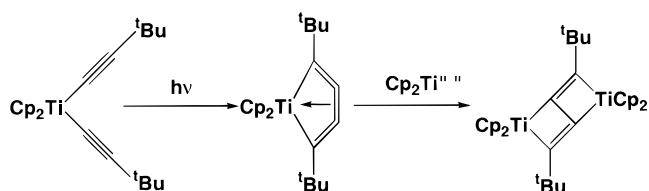
Scheme 14

Scheme 15
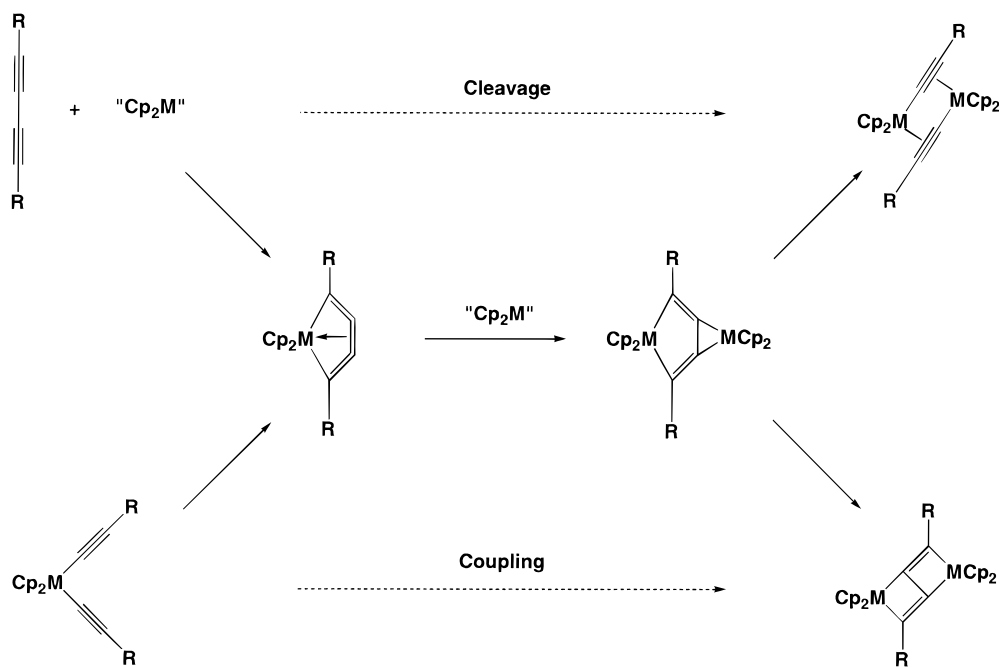
Photochemical Investigations. When a solution of the complex $Cp_2Ti(\sigma\text{-}C\equiv C^tBu)_2$ is irradiated, a titanacyclocumulene is, as shown by NMR spectroscopy, generated in the first step. Consequently, this species reacts with a further equivalent of titanocene to yield the dinuclear complex with $\mu-\eta(1-3),\eta(2-4)\text{-}trans,trans$-butadiene units between two metallocene cores (Scheme 14).[24] This reaction cannot be used preparatively to synthesize the metallacyclocumulenes, as this intermediate is nonisolable.

It remains unclear whether in the first step of the reaction the complex $[Cp_2Ti(\sigma\text{-}C\equiv C^tBu)]$ or the fragment $[Cp_2Ti]$ and the radicals $[^{\bullet}C\equiv C^tBu]$ are formed, as both possibilities could account for the observed reaction course. This reaction was postulated some time ago[27a] and was later found to also occur under the catalytic influence of certain Lewis acids.[27b]

Generalized Reaction Scheme. By taking into account the results of our investigations[24] as well as excellent theoretical calculations,[22] a general simplified scheme is deduced (Scheme 15).[24]

According to this scheme, the cleavage as well as the coupling progresses via metallacyclocumulenes, in which the *intra*molecular coordination of the inner double bond is, in the subsequent step, replaced by an *inter*molecular one. These intermediates then rearrange, depending on the metals M and the substituents R, to afford products in which either an intact or a cleaved C_4 linkage is present. The individual energy levels of these and comparable complexes as well as of the supposed intermediates have been determined by thorough calculations, and the results confirm the relative thermodynamic stabilities as observed experimentally. Thus, these theoretical results emphatically support the documented conceptions about the reaction course.[22]

Photocatalytic C–C Single-Bond Metathesis. A cleavage of various symmetrically substituted butadiynes in combination with a subsequent alternating recombination of the fragments realizes a C–C single-bond metathesis.[28] It is of special note in this context that the first C–C single-bond metathesis reaction ever published has very recently been accomplished using paraffins and immobilized Ta–H catalysts.[29] If one-to-one mixtures of the butadiynes $^tBuC\equiv C\text{-}C\equiv C^tBu$ and $Me_3SiC\equiv C\text{-}C\equiv CSiMe_3$ are treated with an excess of the Cp_2Ti reagent and that mixture is then irradiated, the unsymmetrically substituted diyne $^tBuC\equiv C\text{-}C\equiv CSiMe_3$ is afforded after an oxidative workup, in addition to the symmetrically substituted starting diynes (Scheme 16).

The observed reaction does not work without titanocene. If no irradiation is applied, higher temperatures are essential, and a considerable increase in decomposition reactions is observed. This makes this reaction the first titanocene-mediated, photocatalyzed C–C single-bond metathesis in homogeneous solution.[28] With regard to the metal compound, this metathesis cannot be conducted catalytically, because an excess of the diyne would favor coupling reactions, making those complexes dominant in the product range (see above). The course of the reaction (Scheme 17) can be formulated in such a way that the titanocene reacts with $^tBuC\equiv C\text{-}C\equiv C^tBu$ to form the binuclear complex with an intact C_4 backbone and

Scheme 16
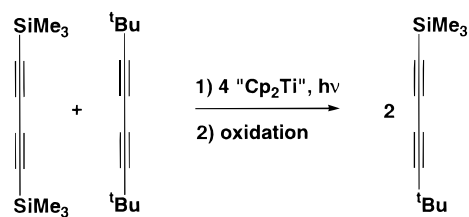
Scheme 17
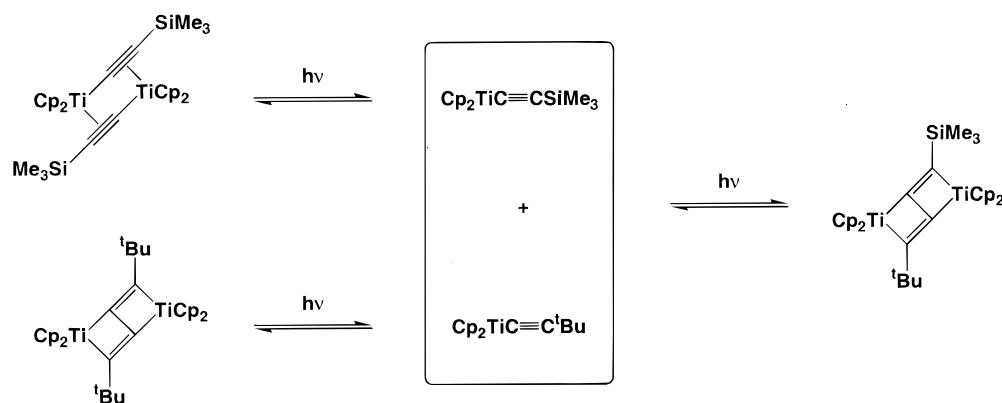
with Me₃SiC≡C−C≡CSiMe₃ to form the σ,π-alkynyl-bridged cleavage product.

Under the influence of light, both 2:1 complexes are subsequently cleaved to the extremely unstable monomeric Ti(III) complexes [Cp₂Ti(σ-C≡C^{t}Bu)] und [Cp₂Ti(σ-C≡CSiMe₃)], which then dimerize to either the respective starting complexes or, in the desired way, to a differently substituted binuclear complex. The reverse reaction can be realized as well. But there remains the drawback of the noncatalytic reaction sequence with respect to the metal compound. As is well established, the use of sterically demanding ligands can often restrict, if not totally avoid, unintentional coupling reactions of the substrates. We therefore conducted experiments, in which the pentamethylcyclopentadienyl ligand (Cp*) was substituted for the cyclopentadienyl ligand (Cp).

Permethylzirconocene and 1,3-Butadiynes. All attempts to realize a catalytic C−C single-bond metathesis of butadiynes using the permethylmetallocene complexes Cp*₂M(η²-Me₃SiC≡CSiMe₃) (M = Ti, Zr) proved unsuccessful, and no stoichiometric products could be recovered in these experimental studies. The unstable monomeric Ti(III) complexes [Cp₂Ti(σ-C≡CR)] seem to play a key role in the reaction sequence of our metathesis reaction. The corresponding permethyltitanocene complexes Cp*₂M(σ-C≡CR) (M = Ti, Zr; R = Ph, ^{t}Bu, SiMe₃) could not be generated via a salt elimination reaction starting from Cp*₂TiX and LiC≡CR. For that reason the stable M(IV) complexes Cp*₂M(σ-C≡CR)₂ (M = Ti, Zr; R = Ph, ^{t}Bu, SiMe₃) were synthesized, and a reduction, which is well-known for the analogous Cp complexes, should have led to the targeted compounds. During the performance of these investigations, it became evident that, for

M = Zr, these complexes very easily rearranged in plain sunlight to afford the zirconacyclocumulenes (Scheme 18).[30]

Additionally, we were able to establish an alternative synthetic route to some novel zirconacyclocumulenes: the reduction of Cp*₂ZrCl₂ with magnesium in the presence of the butadiynes RC≡C−C≡CR (R = Me, Ph, SiMe₃) is suitable to generate the η⁴-complexes (Figure 2), while this does not work for R = ^{t}Bu (compare to Scheme 20).

Permethyltitanocene and 1,3-Butadiynes. Both of the described methods fail to prepare the corresponding titanacyclocumulenes. For R = SiMe₃, a titanacyclopropene, a η²-complex, is formed instead, probably due to steric reasons (Scheme 19).[31]

Manifold C−H activations of the methyl groups of the pentamethylcyclopentadienyl ligand and C−C couplings with the particular diynes have been verified for M = Zr, R = ^{t}Bu; M = Ti, R = ^{t}Bu; and M = Ti, R = Me, Ph (Scheme 20).

These reactions are clearly dependent on the metals M and the substituents R; they are, however, worthless in regard to the synthesis of metallacyclocumulenes and to their application in the catalytic C−C single-bond metathesis. Very interesting, though, are the consecutive reactions of the permethylmetallocene complexes of the butadiynes with carbon dioxide (Scheme 21).
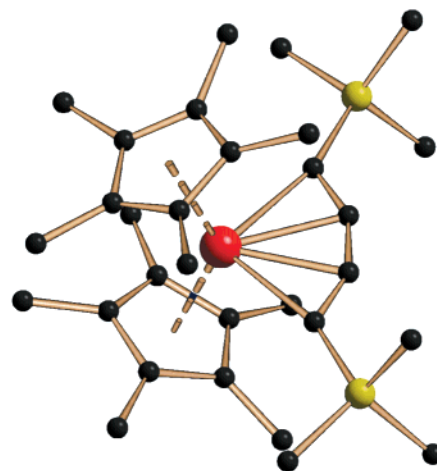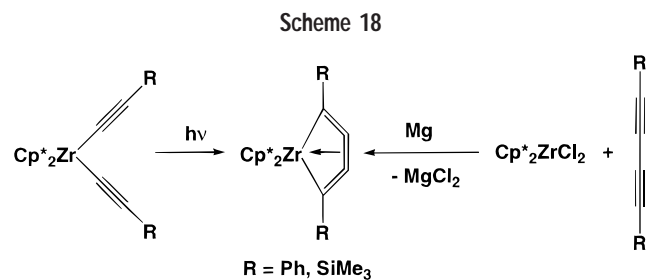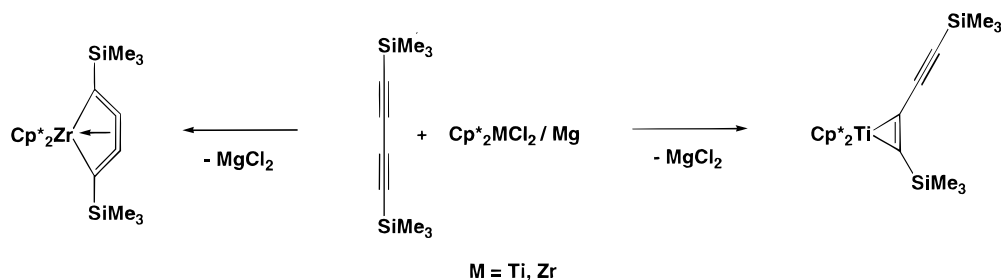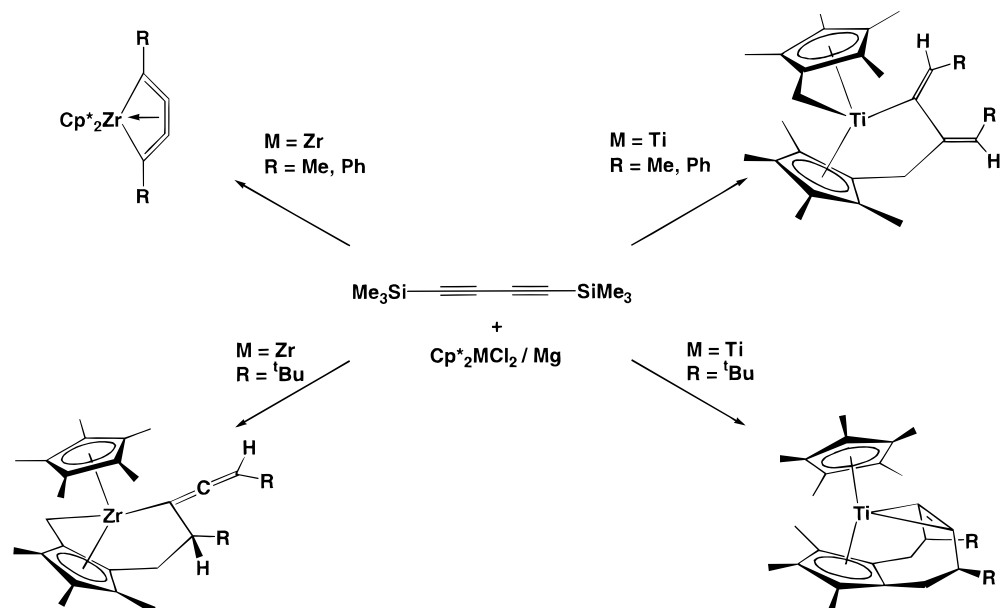
While the zirconacyclocumulene (η⁴-complex) takes up

Scheme 18

R = Ph, SiMe₃

FIGURE 2. Molecular structure of Cp*₂Zr(η⁴-1,2,3,4-Me₃SiC₄SiMe₃).

Scheme 19

M = Ti, Zr

Scheme 20

two molecules of CO$_2$ and thereby forms a cumulenic dicarboxylate (Figure 3), the titanacyclopropene (η^2-complex) inserts only one molecule of CO$_2$ under the formation of a titanafuranone (Scheme 21).

It remains unclear whether the zirconacyclocumulene reacts as a η^4- or a η^2-complex. The reaction course

illustrated in Scheme 21 seems possible. According to that proposal, an analogous zirconafuranone can be formed starting from a η^2-complex, and only for zirconium a further reaction of the alkynyl group in the α-position to the metal is possible.

The insertion of a second molecule of CO$_2$ can also be prevented by employing a sterically very demanding substituent on the diyne (e.g., ^{t}BuMe$_2$Si) (Scheme 22).

Altogether, the stability and reactivity of five-membered metallacyclocumulenes appear to be profoundly influenced by steric factors. These can originate from the steric
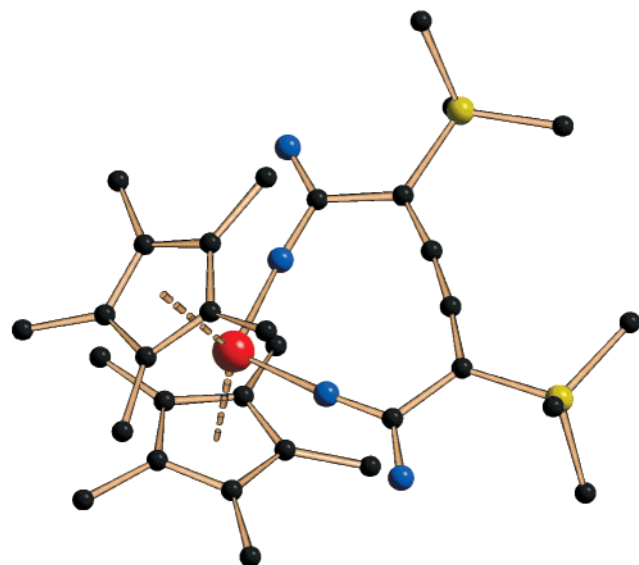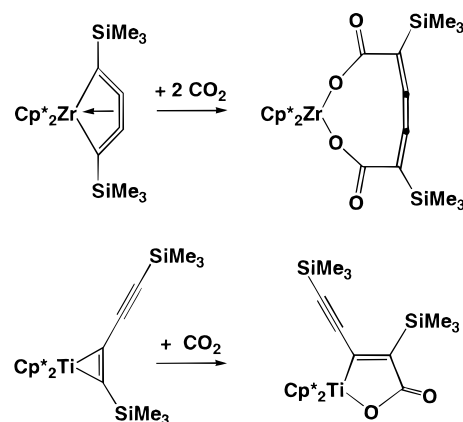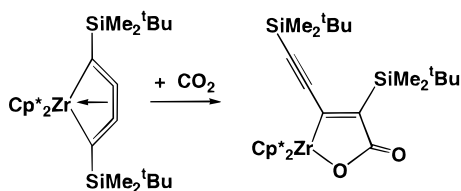

FIGURE 3. Molecular structure of Cp*$_2$Zr[—OC(=O)C(SiMe$_3$)=C=C=C(SiMe$_3$)C(=O)O—].
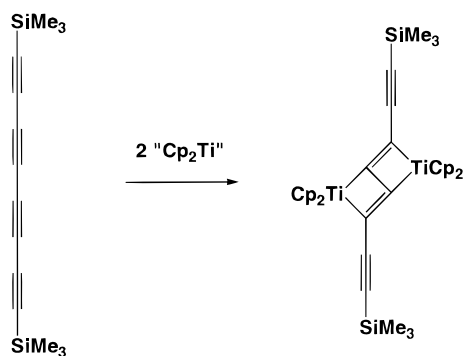
Scheme 21

Scheme 22

Scheme 23

Scheme 24
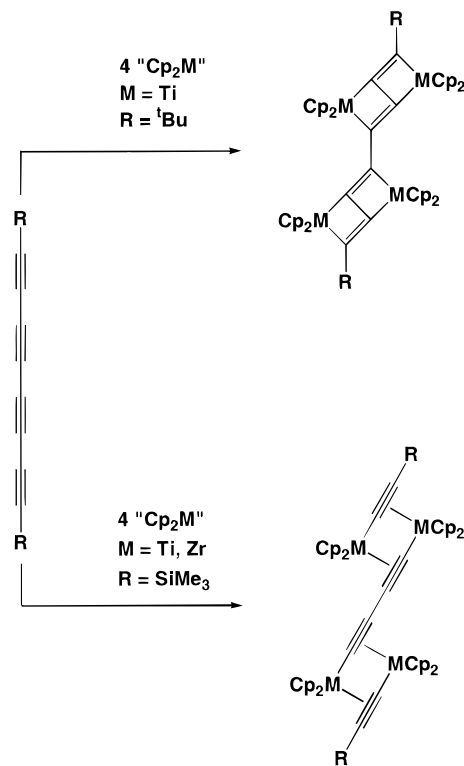
demand of the Cp and Cp* ligands, respectively, and the size of the metal as well as of the substituents attached to the diyne.

Linear and Branched Polyynes. The experiences with the reactions of the alkynes $RC{\equiv}CR$ and 1,3-butadiynes $R(C{\equiv}C)_2R$ with titanocenes und zirconocenes can be used to apply the observed reactivity pattern to oligo- und polyynes, $R(C{\equiv}C)_nR$. In doing this, we aimed at modeling the interactions of group 4 metallocenes with the simplest carbon modification, the "carbyne" $(-C{\equiv}C-)_n$. Principally, one has to differentiate between two reaction pathways: the complexation and the cleavage reactions. In the

conversion of bis(trimethylsilyl)octatetrayne with 2 equiv of titanocene, a complexation is observed, which is shown in Scheme 23.[32]

If 4 equiv of the metallocenes are reacted with the octatetraynes $RC{\equiv}C-C{\equiv}C-C{\equiv}C-C{\equiv}CR$, the products obtained decisively depend on the substituents R and the metals M (Scheme 24).

Scheme 25
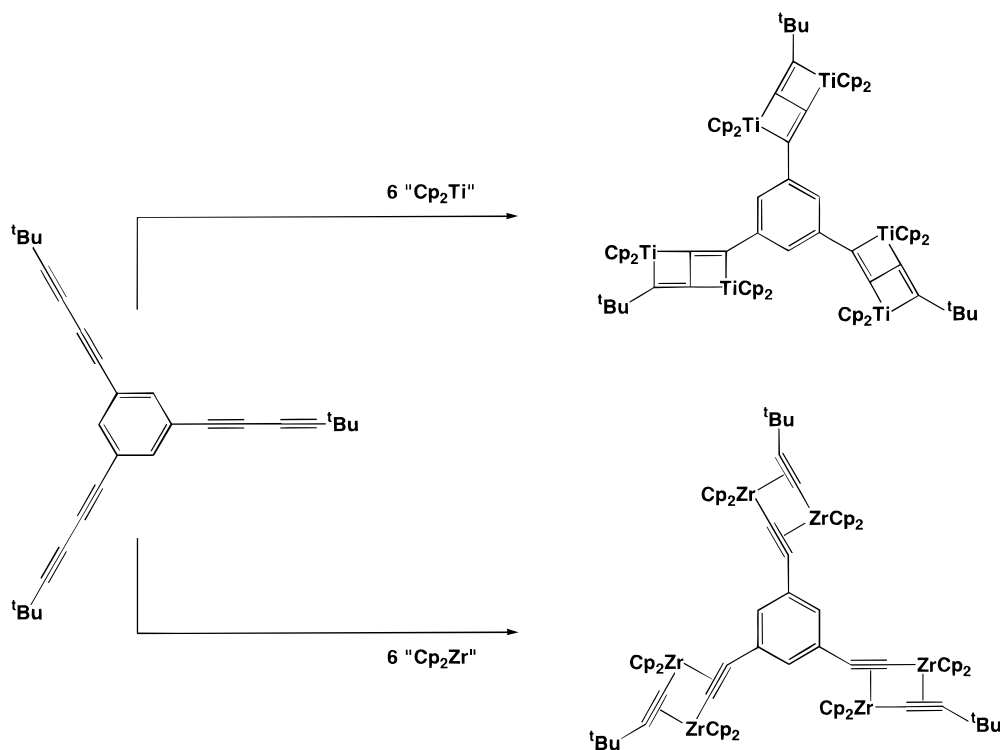
Using $R = SiMe_3$ with the tetrayne, both titanocene and zirconocene lead to complexes in which the two outer C−C single bonds are cleaved (Scheme 24). Changing to $R = {}^tBu$ and applying titanocene, we were able to prevent a cleavage and maintained an intact C_8 backbone in the formed 4:1 complex (Scheme 24).

The found reactivity pattern can also be applied to branched polyynes such as the 1,3,5-tris(*tert*-butylbuta-diynyl)benzene (${}^tBuC\equiv C-C\equiv C)_3C_6H_3$ (Scheme 25).[33]

In the conversions with the metallocenes, we observe a coordination of six titanocene cores to an intact polyyne in the case of M = Ti, while for M = Zr altogether three C−C single bonds are cleaved in the 6:1 complex.

These and related compounds seem to have potential as materials for nonlinear optical devices, in multicenter catalysis, and as precursors for dendrimers.

Conclusions

The metallocene sources $Cp_2M(L)(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ (M = Ti, L = −; M = Zr, L = THF, pyridine) are very suitable and convenient reagents for the investigation of reactions of diynes $R(C\equiv C)_2R$ and polyynes $R(C\equiv C)_nR$ with titanocene and zirconocene. The exceedingly multifaceted chemistry is epitomized by a variety of complexation, coupling, and cleavage reactions of the substrates employed. The course of the reaction can effectively be influenced by varying the metals M, the substituents R, and the stoichiometry. The inquiries into the conversions of simple butadiynes served as a model, and this led to the establishment of the first photocatalyzed C−C single-bond metathesis in homogeneous solution and, additionally, to the application of the observed reactivity pattern to more extensive substrates such as linear and branched oligo- and polyynes. The reactions of the butadiynes have generated some particularly surprising and uncommon structures, of which the metallacyclocumulenes occupy a key role. Even some extensive and profound theoretical studies in that field were initiated by this experimental work. It has repeatedly been proven that the combination of organometallic complexes with suitable substrates very often leads to novel bond types and reactivities.

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