Five-membered metallacycles of titanium and zirconium – attractive compounds for organometallic chemistry and catalysis†

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In these days a renaissance of metallacycles as an increasingly important class of organometallic compounds for synthetic and catalytic applications is evident, making such very attractive for a plethora of investigations. Titanocene and zirconocene bis(trimethylsilyl)acetylene complexes, regarded as three-membered metallacycles (1-metallacyclopropenes), present a rich chemistry towards unsaturated molecules. By elimination of the alkyne these complexes form by reaction with unsaturated compounds five-membered titana- and zirconacycles, all of which are relevant to stoichiometric and catalytic C–C coupling and cleavage reactions of unsaturated molecules.

Introduction

Metallacycles of the transition metal elements have risen since their discovery about half a century ago from lab curiosities to a recognised class of important organometallic compounds. In addition to their multi-faceted structural chemistry they play a significant role in multiple catalytic processes. A recent actual development is dealing with the participation of metallacycles in polymerisation as well as oligomerisation reactions.[1] For example, the selective tri- or tetramerisation of ethylene can in principle proceed *via* formation of chains or *via* metallacyclic compounds, where the latter only recently became increasingly interesting from the point of view of selectivity (Scheme 1).[2]

As part of our intensive studies in the field of five-membered titana- and zirconacycles, we found and established that the corresponding three-membered species are excellent precursors for these enterprises. Titanocene and zirconocene bis(trimethylsilyl)acetylene complexes, $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$, [M = Ti, $Cp'_2 = Cp_2$, Cp^*_2, ebthi and M = Zr, $Cp'_2 = Cp^*_2$, ebthi; Cp: cyclopentadienyl, Cp*: pentamethylcyclopentadienyl, ebthi: 1,2-ethylene-1,1′-bis(tetrahydroindenyl)], best described as 1-metallacyclopropenes, present a rich chemistry towards unsaturated molecules in stoichiometric and catalytic reactions.[3–6] By these investigations it became well established that the bis(trimethylsilyl)acetylene is an excellent spectator ligand that sufficiently stabilizes the metallocene to generate the unstable and reactive core complexes Cp'_2M.

The most important types of symmetrically substituted five-membered metallacycles (with M = Ti, Zr) and some selected methods for their preparation are already summarized in several reviews and represented in Scheme 2.[3–6]

Uwe Rosenthal

Uwe Rosenthal (b. 1950) studied chemistry (1968–72), received his PhD under supervision of Erhard Kurras (1976), and completed his habilitation (1991) at the University of Rostock. After postdoctoral work at the Institute of Organoelement Compounds of the Russian Academy of Sciences in Moscow with Mark E. Vol'pin and Vladimir B. Shur (1988) he became a visiting research scientist at the Max Planck Institute for Coal Research in Mülheim/Ruhr with Günther Wilke and Klaus Pörschke (1990–91). He headed the Max Planck Research Group "Complex Catalysis" (1992–96) and became Professor of Inorganic Chemistry at the University of Rostock (1993). Today he is Deputy Director of the Leibniz Institute for Catalysis. His scientific interests are Organometallic Chemistry and Coordination Catalysis.

Vladimir V. Burlakov

Vladimir V. Burlakov (b. 1955) 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 PhD degree with Mark E. Vol'pin and Vladimir B. Shur. Since 1992, he has spent time on several occasions as a visiting Research Scientist in the Rosenthal group. Now he is the head of a research group at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). His scientific interests are focused on the transformation of unsaturated hydrocarbons and small molecules mediated by Group 4 metal complexes, Ziegler–Natta type catalysts, ring-opening and olefin polymerization.

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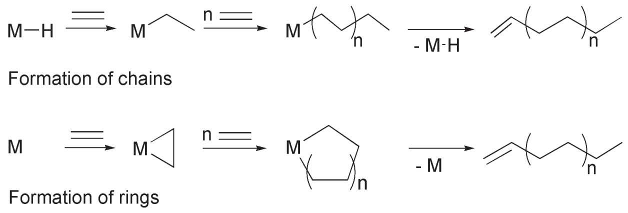
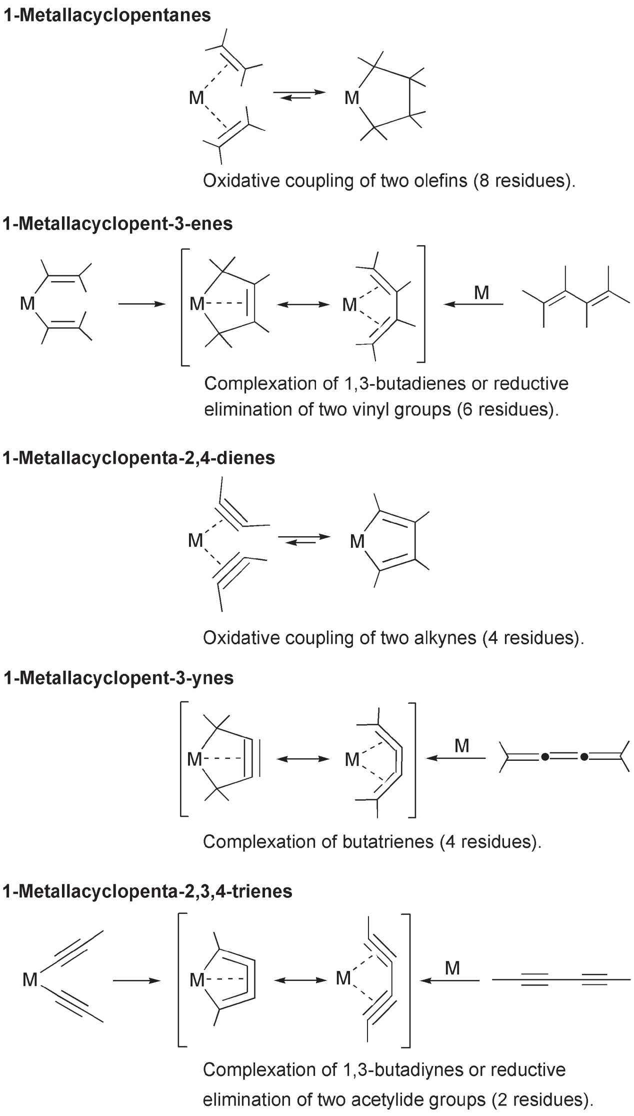
† This Account is dedicated to Professor Vladimir B. Shur on the occasion of his 70th birthday.



Scheme 1 Oligo- and polymerisation of ethene *via* chains or rings.

1-Metalla-cyclopentanes, -cyclopent-3-enes and -cyclopenta-2,4-dienes

These three classes of metallacycles are well investigated and have found use in a growing number of important stoichiometric and catalytic reactions. The chemistry of 1-metallacyclopent-3-enes was extensively studied by the groups of Erker[7] and Nakamura.[8] Very important contributions for the preparation and the synthetic application of 1-metallacyclopentanes and 1-metallacyclopenta-2,4-dienes have been made by Negishi[9] and Takahashi.[10] Compared to the unusual 1-metallacyclopent-3-ynes and 1-metallacyclopenta-2,3,4-trienes (five-membered metallacyclo-cumulenes) these metallacycles show more substituents and a higher degree of saturation, having no, one or two double bonds in the ring system. It is worth mentioning, that the metallacyclopentanes and metallacyclopenta-2,4-dienes in contrast to the metallacyclopent-3-enes undergo cycloreversion reactions under ring opening of the metallacycle, yielding the bis-olefin and bis-alkyne complexes. The insertion of additional unsaturated molecules led to the formation of even larger metallacycles. Another very interesting feature also discussed below is the transition from these metal–all-carbon systems to the corresponding metal–heteroatom–carbon complexes, *e.g.* by coupling of heteroolefins and heteroalkynes. For the 1-metallacyclopent-3-enes as masked 1,3-butadiene complexes the heteroanalogous complexes, *e.g.*, monoaza and diaza butadiene complexes,[11] enediolates *etc.* were also obtained.[12]



Scheme 2 Formation of symmetrical five-membered metallacycles.

Marc Arnold Bach

Marc Arnold Bach (b. 1977) graduated from the Technical University of Kaiserslautern with Jens Hartung (2004) and moved to Rostock for PhD work in the Organometallic Chemistry of titanium and zirconium under supervision of Uwe Rosenthal. In 2005 he became a member of the Research Training Group at the University of Rostock and participated in a DAAD Exchange Programme, spending three months in the group of Eluvathingal D. Jemmis at the Department of Inorganic and Physical Chemistry, Indian Institute of Science in Bangalore. His scientific interests are reactions and calculations of unusual metallacycles.

Torsten Beweries

Torsten Beweries (b. 1982) studied Chemistry (2001–2006) and graduated (2006) from the University of Rostock, completing his Diploma Thesis in the group of Uwe Rosenthal. Recently he started working on his PhD Thesis in the Rosenthal group as a member of the DFG Research Training Group at the University of Rostock. His scientific interests are concentrated on all aspects of modern Organometallic Chemistry and Coordination Catalysis of olefins and alkynes with unusual metallacycles of titanium, zirconium and hafnium.

1-Metallacyclopent-3-ynes

The existence of a 1-titanacyclopent-3-yne structure as an alternative bonding description for the (2-3η)-butatriene complex $Cp_2Ti(\eta^2\text{-}Me_2C{=}C{=}C{=}CMe_2)$, an intermediate in the reaction of $Me_2C{=}C{=}C{=}CMe_2$ and "Cp_2Ti", was first discussed by Maercker *et al.*[13] The first 1-zirconacyclopent-3-ynes were obtained by Suzuki and co-workers in 2002 as a result of the reaction of a zirconocene "Cp'_2Zr" source and 1,4-disubstituted (*Z*)-butatrienes RHC=C=C=CHR (R = Me_3Si, *t*-Bu).[14] Later the 1-zirconacyclopent-3-yne produced by the reaction of Cp_2ZrCl_2 and 1,4-dichlorobut-2-yne with Mg was claimed by Suzuki to be the first "unsubstituted" metallacyclopentyne.[6] The first structurally characterized 1-titanacyclopent-3-yne was obtained by the reaction of two equivalents of the above mentioned titanocene source $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with 1,4-dichlorobut-3-yne in which one "Cp_2Ti" reacts to produce Cp_2TiCl_2 and $H_2C{=}C{=}C{=}CH_2$ and the second complexes the butatriene giving the titanacycle.[15] Meanwhile a large number of other metallacyclopentynes were prepared and investigated with regard to their reactivity.[6]

1-Metallacyclopenta-2,3,4-trienes as stable five-membered metallacyclocumulenes

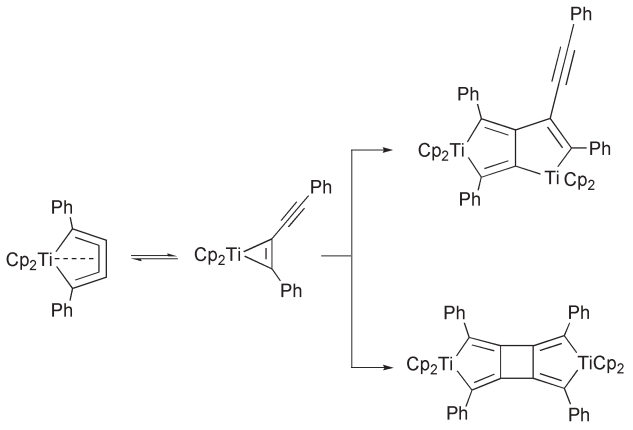
In 1994 the first stable five-membered $Cp_2Zr(\eta^4\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ (1-zirconacyclopenta-2,3,4-triene, η^4-butadiyne complex) was obtained from $Cp_2Zr(pyridine)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ by replacement of pyridine and bis(trimethylsilyl)acetylene by 1,3-butadiyne *t*-BuC≡C–C≡C-*t*-Bu.[16] Later the titanacyclocumulenes $Cp_2Ti(\eta^4\text{-}RC_4R)$ with R = *t*-Bu and Ph also were obtained by a similar procedure starting from $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and RC≡C–C≡CR.[6] After irradiation of the titanium bis-acetylides such as $Cp_2Ti(\sigma\text{-}C{\equiv}C\text{-}t\text{-}Bu)_2$, the five-membered titanacyclocumulene $Cp_2Ti(\eta^4\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ was detected by NMR spectroscopy as an intermediate which rapidly reacted with additional titanocene "Cp_2Ti" to give a dinuclear complex with a bridging 1,3-butadiyne.[6] This type of reaction in which 1,3-butadiyne complexes are formed upon irradiation was first postulated in 1986 by Frömberg in the Erker group[17] and was later confirmed by Erker *et al.* to occur under the catalytic influence of certain Lewis acids, too.[18] Surprisingly, the exposure of the simple complexes $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$, R = Ph, $SiMe_3$, Me, to sunlight resulted in C–C coupling of the alkynyl groups to give the unusual zirconacyclocumulenes $Cp^*_2Zr(\eta^4\text{-}RC_4R)$, R = Ph, $SiMe_3$, Me, in high yields.[19] Some of these complexes were also prepared by the reduction of $Cp^*_2ZrCl_2$ with magnesium in the presence of the corresponding diynes RC≡C–C≡CR. The synthesis and chemistry of the mentioned metallacyclocumulenes were summarized in several reviews.[3–6]

Structure and bonding of metallacyclopentynes and metallacyclocumulenes

The structures of the metallacyclopentynes and metallacyclocumulenes are in principle very similar. Both show an almost planar arrangement of the metallacycle with one C–C triple or three C–C double bonds.[6,20–22] The central unsaturated bond is elongated which can be ascribed to its intramolecular interaction with the metal center. In metallacyclocumulenes the other double bond distances are close to those calculated for the metal-free carbon cyclopenta-1,2,3-triene. In contrast, the corresponding angles in the complexes are different from those calculated for the all-carbon cycle. In the structures of the unsubstituted 1-metallacyclopent-3-ynes the triple bonds (Ti: 1.248(4); Zr: 1.237(3) Å) correspond very well to the calculated 1.226 Å in the metal-free cyclopentyne and are shorter compared to the central double bonds in metallacyclocumulene examples (Ti: 1.339(13); Zr: 1.31(1) Å).[6] A new diffraction study using synchrotron radiation showed a longer triple bond (1.250(3) Å) for the 1-zirconacyclopent-3-yne compared to what was determined by the conventional X-ray analysis.[23]

First theoretical calculations from Jemmis and co-workers did actually show that titana- and zircona-cyclocumulenes are thermodynamically more stable compared to the isomeric bis σ-acetylide complexes.[6,20] All four carbon atoms of the former diyne have p orbitals occupied by one electron perpendicular to the plane of the metallacycle. The sp hybridized internal C atoms possess additional p orbitals in that plane, which are used for donor bonding to the metal center. The calculated bond distances and angles were in good agreement with the experimental values.[20,21] Additionally, Jemmis *et al.* used DFT calculations for metallacyclocumulenes in connection with the Dewar–Chatt–Duncanson model. For a late metal complex, the hypothetical "nickelacyclocumulene" the central C–C bond was calculated to be longer than the other two C–C bonds having back-bonding interaction between the filled metal d orbitals and the in-plane empty π^* orbital of the middle C–C bond.[6,21]

Other DFT studies of the energetics of the metal-free C_5H_4-cyclocumulene and the organometallic analogs obtained by replacing the CH_2 groups by the metallocenes Cp_2Ti and Cp_2Zr showed that the relative energies of the compounds are dramatically altered in the transition-metal analogues. The metallacyclocumulenes are comparable in energy to the metallacyclopropenes and the bis-alkynyl complexes. After results from Jemmis *et al.* and Jiao the bonding situations in the metallacyclocumulenes and the metallacyclopentynes are very similar.[21] A strong delocalisation in both metallacycles was identified with the metallacyclocumulenes being "in plane aromatic" and the zirconacyclopentynes being "neutral bishomoaromatic". Yet another comparison of both types of metallacycles was drawn by Lin *et al.*, who suggested that the zirconocene complex is better described by resonance hybrids involving a metallacyclopentyne and a butatriene complex Lewis structure.[22] From isodesmic reactions he concluded that the cumulene complex description contributes significantly to the stability of these complexes. The perception as a metallacyclopentyne structure alone could not describe sufficiently the structural behavior and the stability of the complex. According to the above mentioned recent experimental electron density study of the 1-zirconacyclopent-3-yne the system can be characterized by a resonance hybrid between the (η^2, σ, σ)- and (η^2, π, π)-coordination in which the latter is the major contribution.[23] Additionally, an "in plane"



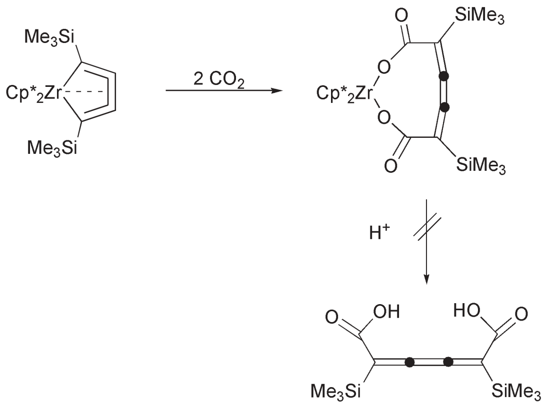
Scheme 3 Coupling of a metallacyclocumulene.

π-delocalization of the Cβ–Cβ′ bond over the Cα–Cβ bond was proposed, but these suggestions do not agree with the calculations from other groups. Several comparable papers with regard to calculations of these interesting metallacycles were already published. Nevertheless, the real bonding situation in metallacyclopentynes and metallacyclocumulenes with its consequences for their reactivity is not yet fully clarified. Mesomerism of metallacycles and π-complexes as well as an equilibrium between η^2- and η^4-coordination complicate the understanding.[6] In addition, certain influences from Cp′ and M lead to small but significant differences for these systems.

Metallacyclocumulenes and metallacyclopentynes – general reaction behavior

In several reactions of the metallacyclocumulenes an equilibrium between an η^4-complex (metallacyclocumulene) and an η^2-complex (metallacyclopropene) was found.[6] One example described the reaction of two complexes of the equilibrium mixture with each other to afford a symmetric and an unsymmetric coupling product. The unsymmetric complex consists of a titanacyclopentadiene which is anellated to a titanacyclopentene (Scheme 3). Its formation can be rationalized by an insertion of the internal double bond of the titanacyclocumulene into a Ti–C bond of the titanacyclopropene.[6] The symmetric complex is a symmetrically substituted titanium radialene which is generated by formal dimerization of two titanacyclocumulene molecules.

The reactions of titanacyclocumulenes with acetone and water yielded insertion products which can only result from the reaction of the η^2-complex (metallacyclopropene).



Scheme 5 Carbon dioxide insertions into a zirconacyclocumulene.

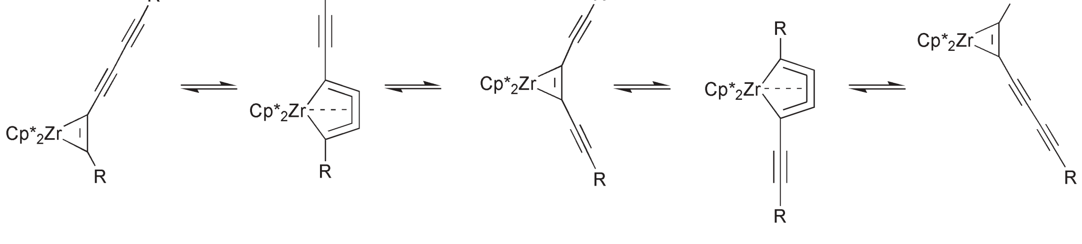
For triyne complexes of Zr the process of alternation between a η^4-complex and a η^2-complex can lead to an interesting "sliding" of the "Cp^*_2Zr" along the carbon chain including the formation of metallacyclocumulenes (Scheme 4).[24]

The zirconacyclocumulene $Cp^*_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$ reacted with two equivalents of carbon dioxide to form a cumulenic dicarboxylate by a formal twofold insertion into the η^4-complex.[6] It remains unclear whether the metallacyclocumulene reacts as an η^4- or an η^2-complex. Acidolysis of the insertion product did not yield the corresponding [3]cumulenic dicarboxylic acids or esters (Scheme 5).

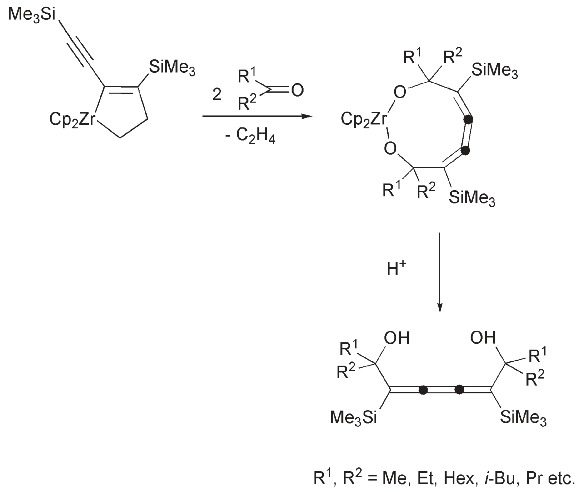
Very recently Liu and co-workers described an elegant route to *cis*-[3]cumulenic diols by the reaction of alkynylated zirconacyclopentenes with ketones for which zirconacyclocumulenes were assumed as intermediates (Scheme 6). This reaction is related to the carbon dioxide insertion mentioned above.[25]

Suzuki proposed that in the *cis*/*trans*-isomerisation of substituted zirconacyclopentynes changing of hapticity also occurs similarly to that described for the metallacyclocumulenes with an equilibrium between an η^4-complex (metallacyclocumulene) and an η^2-complex (metallacyclopropene). The latter species of the equilibrium mixture can react under β-hydrogen elimination and re-insertion (Scheme 7).[14]

Acidolysis of the zirconacyclopent-3-ynes gave the 1,4-disubstituted 2-butynes and no other products (Scheme 7). This result is an argument to understand these compounds as real metallacycles and not as π-complexes. There is no evidence indicating an insertion or a [2+2] cycloaddition of these zirconacyclopentynes with olefins. Nevertheless, Suzuki has found (Scheme 8) in the reaction of the "Takahashi reagent"



Scheme 4 Sliding of a zirconocene along the backbone of a triyne.



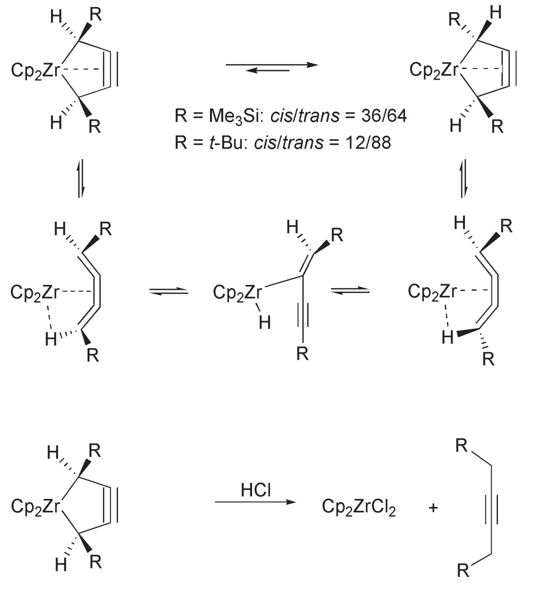
R^1, R^2 = Me, Et, Hex, *i*-Bu, Pr etc.

Scheme 6 Formal ketone insertions into a zirconacyclocumulene.

with butatrienes a formal ethylene insertion product. Similar products were obtained by using the "Negishi reagent" and Me$_3$SiC≡CMe. For both cases it remains unclear if in the reaction mixture zirconacyclopentynes are involved (Scheme 8).[26]

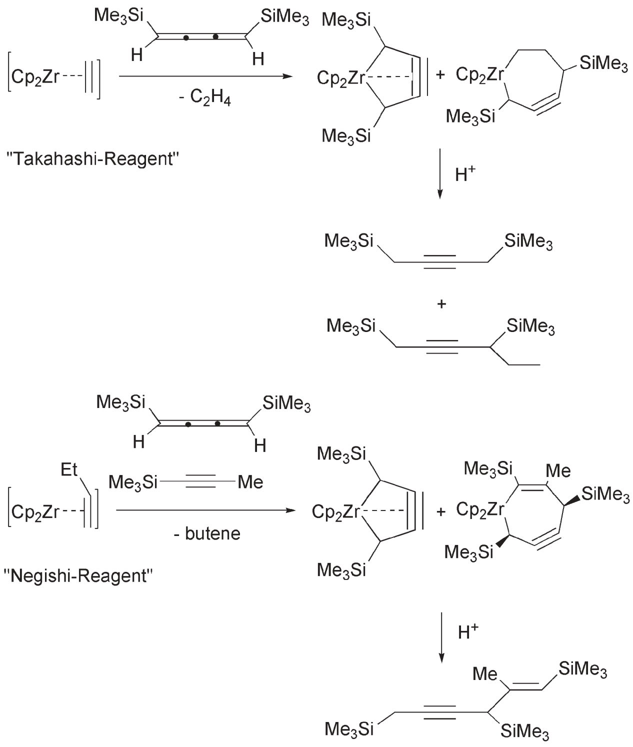
Metallacyclocumulenes and metallacyclopentynes – reactions with Lewis acids

Depending on the substitution pattern, the five-membered zirconacyclocumulenes Cp$^*_2$Zr(η^4-1,2,3,4-RC$_4$R) (with R = Me$_3$Si, Me, Ph) react differently with B(C$_6$F$_5$)$_3$ (Scheme 9).[4,6] For R = Me$_3$Si a catalytic bond cleavage of the central carbon–carbon double bond of the cyclocumulene was found, followed by formation of the bis-σ-alkynyl complex Cp$^*_2$Zr(σ-C≡CSiMe$_3$)$_2$. This process is interesting, because the reverse reaction of the coupling of acetylides to cumulenes was realised, too.[4,6,18] An explanation for this reaction behaviour can be found in the varying influences that were exerted by Cp′ and alkynyl substituents (Cp′ = Cp and R = Me: coupling; Cp′ = Cp* and R = Me$_3$Si: cleavage). With R = Me the B(C$_6$F$_5$)$_3$ group attacks the β-C-atom of the cumulene under ring opening, yielding a product with a σ-bonded intact C$_4$-chain, whose triple bond back-coordinates the Zr metal center. With R = Ph no cleavage of the C$_4$-chain is observed, but B(C$_6$F$_5$)$_3$ attacks the α-C-atom of the cumulene, resulting in the formation of a 1,4-diphenylbuta-1,2,3-triene-1-yl-4-[tris(pentafluorophenyl)borate] ligand.[4,6]

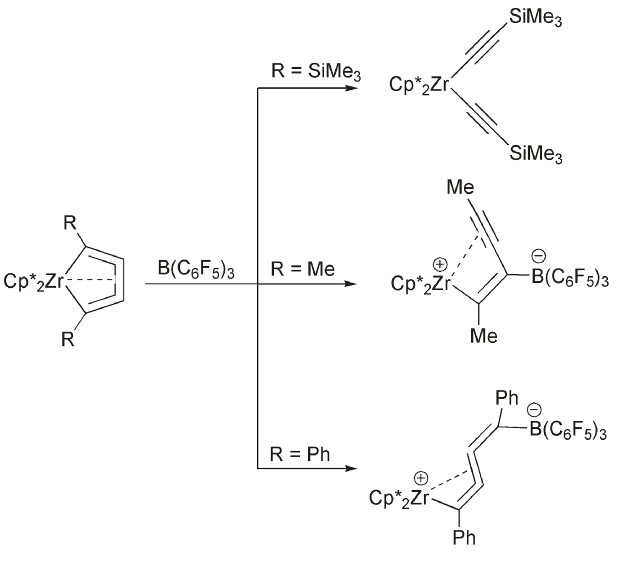


R = Me$_3$Si: *cis*/*trans* = 36/64
R = *t*-Bu: *cis*/*trans* = 12/88

Scheme 7 Isomerization and acidolysis of zirconacyclopentynes.



Scheme 8 Formal olefin and alkyne insertion into a zirconacyclopentyne.

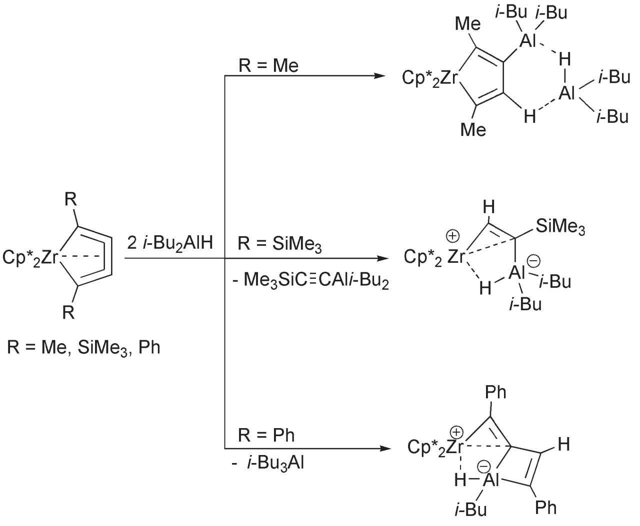


Scheme 9 Reactions of zirconacyclocumulenes with B(C$_6$F$_5$)$_3$.

The metallacyclopentynes react with $B(C_6F_5)_3$ under ring opening of the metallacycle and formation of the zwitterionic complexes $[Cp'_2M]^+-CH_2C{\equiv}CCH_2-[B(C_6F_5)_3]^-$ (Scheme 10).[27]

It should be stated that the course of reaction for metallacyclocumulenes and metallacyclopentynes with $B(C_6F_5)_3$ is similar to what was found by Erker and co-workers for the metallacyclopentenes.[7,27] These ring opening reactions leading to zwitterionic complexes where the counter-anion is tethered to the end of the growing chain adopt an important role in highly active single component catalysts for olefin polymerisation.

By the reaction of the zirconacyclocumulenes with *i*-Bu_2AlH active catalysts for olefin polymerisation are also formed.[4] For R = Me the initial *cis*-hydroalumination of the central double bond gave a zirconacyclopentadiene with an *i*-Bu_2Al substituent in the 3-position as an intermediate, that was stabilized by a second molecule of *i*-Bu_2AlH. With R = Me_3Si the central C–C bond was cleaved ("hydroaluminolysis") under formation of the alkyne *i*-$Bu_2AlC{\equiv}CSiMe_3$ and the alkyne complex $[Cp^*_2Zr(\eta^2\text{-}Me_3SiC{\equiv}CH)]$. The latter was stabilized by subsequent reaction with *i*-Bu_2AlH to give a heterobimetallic ZrAl-complex. In the case of R = Ph a heterobimetallic ZrAl-complex was formed by interaction with *i*-Bu_2AlH and elimination of *i*-Bu_3Al (Scheme 11).

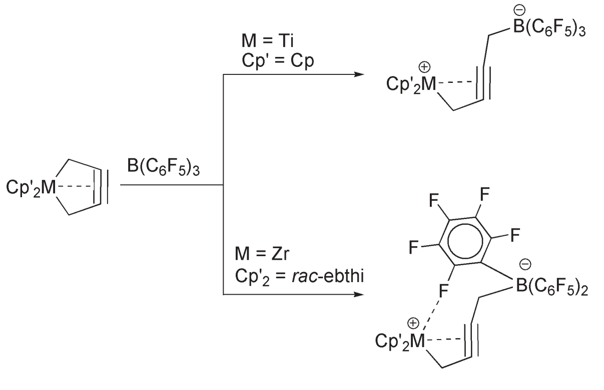


Scheme 11 Reactions of zirconacyclocumulenes with *i*-Bu_2AlH.

1,3-Butadiynes and 1,2,3-butatrienes as bridging ligands

Metallacyclocumulenes and metallacyclopentynes are able to coordinate with their unsaturated bonds to other metals in order to form binuclear complexes (Scheme 12).[6] These complexes represent compounds with either "*cis*"- or "*trans*"-complexation of the unsaturated compounds. By "*cis*"-complexation with M′ = Ni(0), the metallacyclopentynes form metallacyclopentene complexes and the metallacyclopentatrienes yield metallacyclopentadienes.[6]

It is well established that two "titanocene" units and diverse butadiynes yield binuclear complexes like μ-η(1-3),η(2-4)-*trans*,*trans*-tetradehydrobutadiene with intact C_4-units between the two metallocene centers, a structural feature that is unknown for "zirconocene". The same complexes are formed by reaction of titanacyclocumulenes with "titanocene" showing a "*trans*"-complexation of the diynes – also known as "zigzag-butadiene ligands" (Scheme 12).[6]

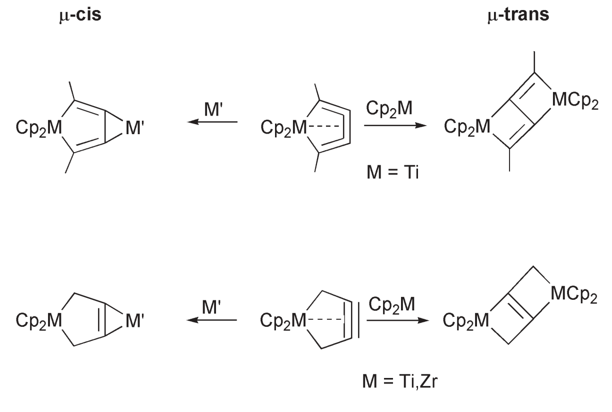


Scheme 10 Reactions of metallacyclopentynes with $B(C_6F_5)_3$.

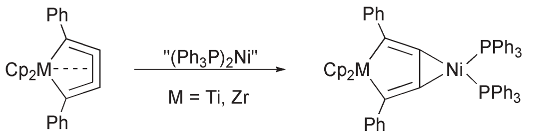
Reaction of zirconacyclocumulenes with additional "zirconocene" does not result in the formation of these complexes; the diynes are cleaved under formation of $[Cp'_2Zr]_2$-μ-(σ,π-$C{\equiv}CSiMe_3)_2$. The metallacyclopentynes react with metallocenes "Cp_2M" to give μ-"*trans*"-butatriene complexes, which are better described as dimetallabicycles (2,5-dimetallabicyclo[2.2.0]hex-1(4)-enes). Complexes of this type were found for Ti and Zr and they are analogous to the above mentioned μ-"*trans*"-butadiyne complexes (Scheme 12).[6]

Certain metallacyclocumulenes coordinate Ni(0) fragments to give stable complexes of the type $Cp_2M[\mu(\eta^4\text{-}PhC_4Ph)]Ni(PPh_3)_2$.[6] These π-complexes of metallacyclocumulenes were isolated for M = Ti and Zr as Ni(0) complexes of the type $(Ph_3P)_2Ni$(cycloolefin). These compounds represent stable complexes of η^2-metallacyclopentatrienes (Scheme 13).

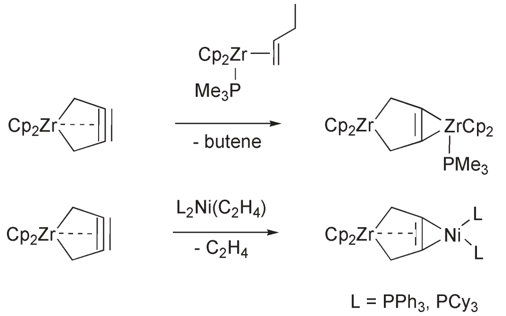
The 1-zirconacyclopent-3-yne forms a cycloalkyne complex with "$Cp_2Zr(PMe_3)$", containing a C_4-unit between the metals, described as a 1-zirconacyclopent-3-ene (Scheme 14).[6,28] The unsubstituted 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$ reacts in a similar manner with the nickel(0) complexes $L_2Ni(\eta^2\text{-}C_2H_4)$ (L = PPh_3 or PCy_3) to give the analogous



Scheme 12 Complexation of metallacyclocumulenes and -pentynes.



Scheme 13 *cis*-Complexation of metallacyclocumulenes.



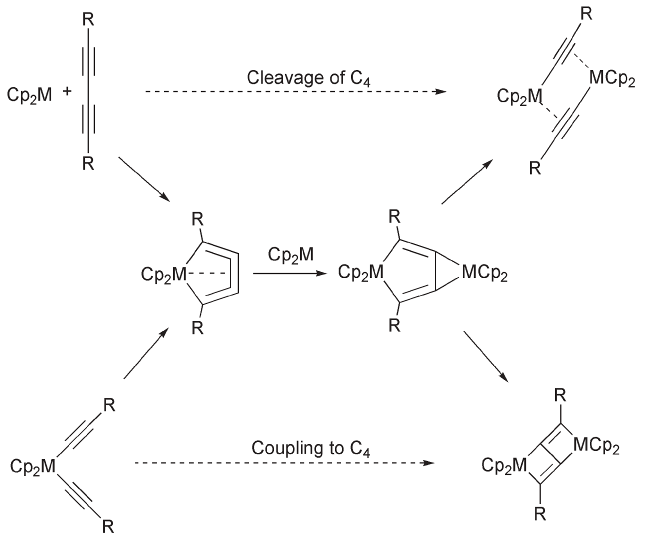
Scheme 14 *cis*-Complexation of zirconacyclopentynes.

binuclear complexes $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]NiL_2$ (L = PPh_3 and PCy_3) (Scheme 14).[28] The formed 1-zirconacyclopent-3-ene unit in these complexes is not planar.

However, the structural comparison of the zirconacyclocumulene $Cp_2Zr[\mu(\eta^4\text{-}PhC_4Ph)]Ni(PPh_3)_2$ ('a') with the zirconacyclopentyne complex $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]Ni(PPh_3)_2$ ('b') shows, that the CαCβ and the Cα′Cβ′ bond lengths in 'a' possess double bond character whereas the corresponding bonds in 'b' can be regarded as single bonds. Furthermore, the CβCβ′ bond length in 'a' are typical for Ni(0) olefin complexes and in 'b' characteristic for Ni(0) alkyne complexes.[6,28]

In the metallacyclocumulene complex the coordinated cyclopentatriene adopts together with the nickel atom a plane whereas the angle between the plane ZrCαCα′ and CαCβCβ′Cα′ is 25.6° in the metallacyclopentyne complex. This indicates that the metallacyclopentyne complexes act as "metallacyclopentenes" with a typical additional interaction of the remaining double bond with the zirconium. In the above mentioned metallacyclopentyne complex $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2C_4H_2)]ZrCp_2(PMe_3)$ the formed "metallacyclopentene" was reported to be "flat". The difference between both complexes is explained by a stronger interaction of the triple bond with the second zirconium in this complex ($4e^-$ ligand) compared to a weaker interaction of Ni(0) in the complex $Cp_2Zr[\mu(\eta^4\text{-}H_2C_4H_2)]Ni(PPh_3)_2$ ($2e^-$ ligand). Contrarily, the 1-titanacyclopent-3-yne $Cp_2Ti(\eta^4\text{-}H_2C_4H_2)$ did not show such a complexation with $L_2Ni(\eta^2\text{-}C_2H_4)$.[6,28]

The Ni(0) metallacyclocumulene complexes prove the metallacyclocumulene structure of the η^4-complex and are intermediates for the cleavage reactions to doubly σ,π-alkynyl-bridged homo- and heterobinuclear metal complexes (Scheme 15). It was shown by mass spectroscopy that the binuclear complexes with intact C_4-units can form unstable monomeric Ti(III) monoacetylides [$Cp_2Ti(\sigma\text{-}C\equiv CR)$]. Such Ti(III) complexes are indeed stable and isolable in the case of decamethyltitanocene complexes $Cp^*_2Ti(\sigma\text{-}C\equiv CR)$ with R = Me or *t*-Bu. With R = Me_3Si they dimerize to doubly σ,π-alkynyl-bridged titanocene complexes. Such a cleavage reaction of the former 1,3-butadiynes can also be called dichotomy [dichotomia, διχοτομία = cut in half].[6,28]



Scheme 15 Metallacyclocumulenes as key intermediates in cleavage and coupling reactions.

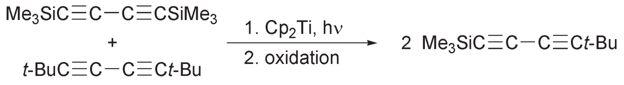
Coupling and cleavage reactions for 1,3-butadiynes

The coupling to and the cleavage of 1,3-butadiynes proceeds *via* metallacyclocumulenes which interact with transition metal complex fragments or a Lewis acid. By this process the intramolecular coordination of the central double bond of the cyclocumulene is converted to an intermolecular coordination. Starting from the formed μ-"*cis*"-butadiyne complexes these intermediates rearrange to products with cleavage or retention of the C_4 chains (Scheme 15).

In principle such a sequence of reactions should be possible for the corresponding butatrienes and metallacyclopentynes, too. Unfortunately, there is only a very small number of examples for the coupling of vinylidene ligands to butatrienes.[29] To the best of our knowledge no examples for the reverse cleavage of butatrienes (maybe *via* metallacyclopentynes and its interaction with metals) have been found yet.

C–C Single bond metathesis

Cleavage of two symmetrically substituted 1,3-butadiynes to acetylides and subsequent alternating recombination of the acetylide fragments realizes an unusual C–C single bond metathesis. When mixtures of *t*-BuC≡C–C≡C-*t*-Bu and $Me_3SiC{\equiv}C\text{–}C{\equiv}CSiMe_3$ were treated with four equivalents of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ as a source of "Cp_2Ti" and irradiated, *t*-BuC≡C–C≡CSiMe$_3$ was obtained after oxidative work-up, in addition to unreacted starting material (Scheme 16).[3–6]



Scheme 16 C–C single bond metathesis of butadiynes.

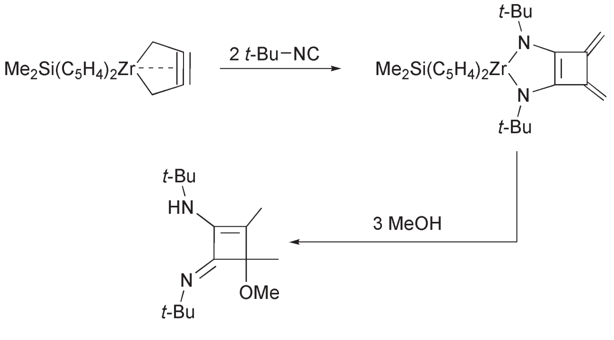
This titanocene-mediated photolytic C–C single bond metathesis in homogeneous solution did not proceed without titanocene or without irradiation. This metathesis cannot be conducted with catalytic amounts of Cp_2Ti, because an excess of the diyne favored varying coupling reactions to titanacyclopentadienes.

In this reaction the titanocene forms with t-BuC≡C–C≡C-t-Bu the titanacyclocumulenes ("*cis*" butadiyne complexes) which interacts with further titanocene to the binuclear "*trans*"-butadiyne complex with an intact C_4 backbone. $Me_3SiC≡C–C≡CSiMe_3$ *in situ* also forms the titanacyclocumulene, which then transforms into the σ,π-alkynyl bridged complex. Both dinuclear complexes are cleaved under the reaction conditions giving the unstable, monomeric Ti(III) acetylides [Cp_2Ti(σ-C≡C-t-Bu)] and [Cp_2Ti(σ-C≡$CSiMe_3$)]. Homo- or heterodimerization of these reactive species produced the starting material or the binuclear metathesis product. Such a reaction pathway should in principle be envisioned for butatrienes *via* metallacyclopentynes, too.[29]

Concept and outlook:

Complexation of 1,3-heterobutatrienes and formation of 1-metalla-2,5-heterocyclopent-3-ynes?

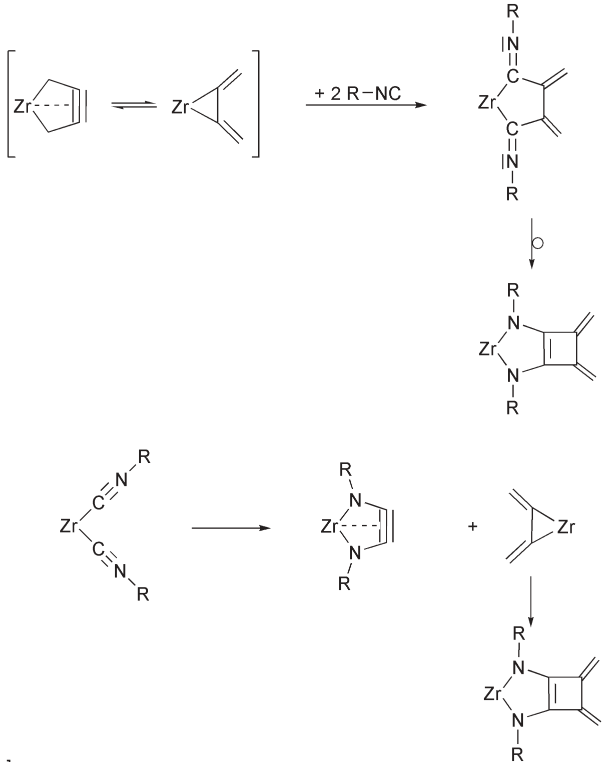
Recently, we've found an interesting result when reacting a zirconacyclopentyne with an isocyanide, a reaction, in which formally two molecules of the isocyanide (t-Bu–NC) should insert into the β-Zr–C bonds of the zirconacycle. After subsequent stabilization a substituted 1-zircona-2,5-diazacyclopent-3-ene, anellated with a cyclobutene ring having two exocyclic double bonds, was finally obtained, giving the metal-free cyclobutene after protolysis with MeOH (Scheme 17).[30]



Scheme 17 Isocyanide insertions into a zirconacyclopentyne.

To explain the formation of this unusual product one can consider either the insertion reaction of the isocyanides into a (2-3η) butadiene complex and its subsequent stabilization by rearrangement or alternatively a coupling of two isocyanides to a 1-zircona-2,5-diazacyclopent-3-yne which would react with the butadiene (Scheme 18).

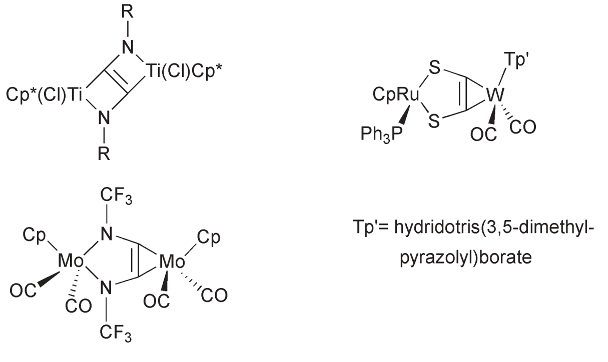
The unusual coupling of the isocyanides leads to the question about the existence of a 1-zircona-2,5-diazacyclopent-3-yne. At first sight such a molecule appears to be very unusual, but as for the 1,3-butadiene complexes (metallacyclopentenes) for which monoaza- and diazabutadiene analogues are well known, the discussion for the butatriene complexes (metallacyclopentynes) can be extended to the isolobal elementorganic compounds, too.



Scheme 18 Alternative mechanistic suggestions for the formation of the isocyanide insertion product.

It is true that for the case of mononuclear compounds this type of complex was not described, but Hessen and co-workers published an interesting coupling of two isocyanides to a μ-"*trans*"-diazabutatriene complex of the heterocumulene RN=C=C=NR, which is very similar to the already discussed μ-"*trans*"-butatriene titanium complex.[31] In that paper the authors outlined the similarities to the coupling reaction of acetylides to 1,3-butadiynes and their complexation (Scheme 19).

For molybdenum Lentz *et al.* described a dinuclear complex by coupling two F_3C–NC molecules between the two metal atoms. One can understand this structure as μ-"*cis*"-diazabutatriene complex which is very similar to the above discussed



Scheme 19 Examples of 1-metalla-2,5-heterocyclopent-3-yne complexes.

μ-"*cis*"-butatriene metal complexes (Scheme 12) as a complex of a 1-molybdena-2,5-diazacyclopent-3-yne (Scheme 19).[32]

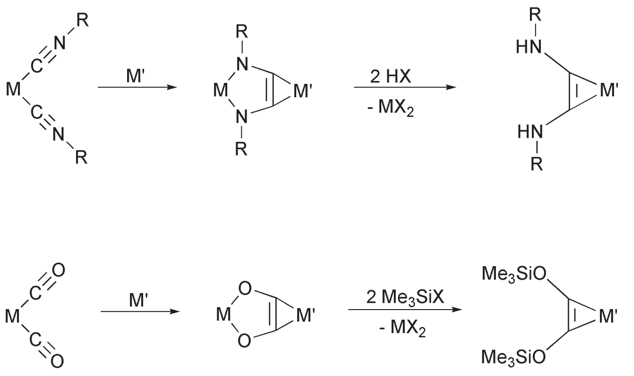
Seidel *et al.* found a dinuclear complex which formally consists of a 1-ruthena-2,5-dithiacyclopent-3-yne which is complexed by tungsten (Scheme 19).[33]

The formation of diaminoalkyne complexes by coupling of isocyanides, described and mechanistically investigated by the group of Lippard and others[34] could in principle be transferred to other systems and the early transition metals *via* the 1-metalla-2,5-diazacyclopent-3-ynes discussed herein. Upon formation following the discussed pathway, these species (as described above for the 1-zirconacyclopent-3-ynes, Scheme 7, but without decomplexation of the formed alkyne) would give the diaminoalkyne complexes after partial hydrolysis (Scheme 20).

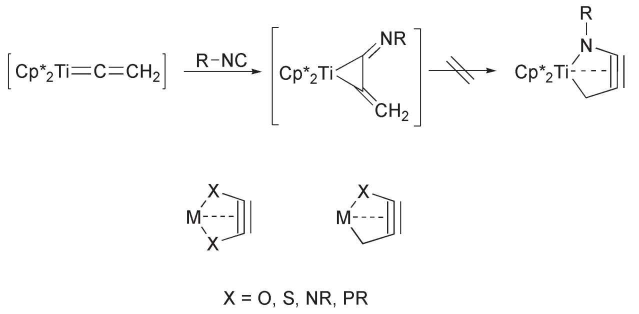
The basic investigations described herein, paved the way to a new approach for unusual reductive coupling reactions with small monomers, *e.g.*, of carbon monoxide to dihydroxyacetylene complexes and of isocyanides to diaminoacetylenes[34] *via* the formation of 1-metalla-2,5-diheterocyclopent-3-ynes and stabilization by a second metal center. Quenching reactions of these proposed intermediates with water or Me_3SiCl should yield complexes of $RNHC{\equiv}CNHR$ or $Me_3SiOC{\equiv}COSiMe_3$, molecules that were too reactive to be easily prepared otherwise.

This chemistry is not restricted to symmetric heterocumulenes as shown by Beckhaus and co-workers,[35] discussing similar species $[Cp^*_2Ti(\eta^2\text{-}H_2C{=}C{=}C{=}NR)]$ in the reaction of $[Cp^*_2Ti{=}C{=}CH_2]$ with R–NC. A 1-titana-2-azacyclopent-3-yne was not discussed for the Cp^*_2Ti fragment, but could be relevant for the unsubstituted Cp analog (Scheme 21).

All these examples as structures of "*trans*"- and "*cis*"-2,5-diheterobutatriene complexes give the impression of the metallacyclopentynes as being not so unusual building blocks. The question emerges as to whether other complexes of this type can be formed with, *e.g.* N, P, O, S atoms in the metallacyclic ring system by complexation of the elementorganic heterobutatriene species such as $R_2C{=}C{=}C{=}X$, $X{=}C{=}C{=}X$; X = O, S or $R_2C{=}C{=}C{=}XR'$, $RX{=}C{=}C{=}XR'$; X = N, P (Scheme 21).



Scheme 20 Description of an alternative mechanism for the coupling of isocyanides and carbon monoxide with 1-metalla-2,5-heterocyclopent-3-yne complexes as intermediates.



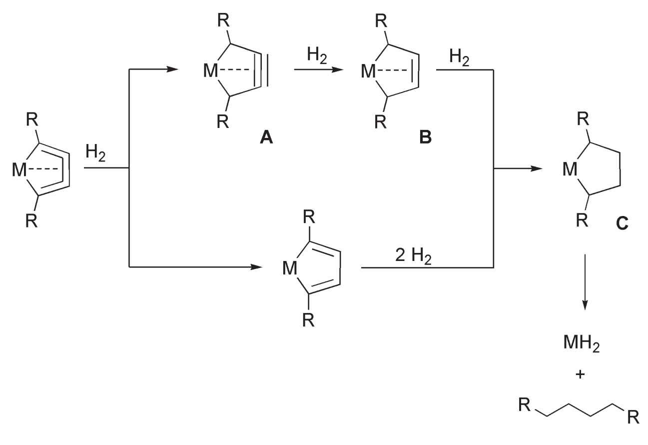
Scheme 21 1-Metalla-2-mono- and -2,5-diheterocyclopent-3-ynes.

Structural relations between metallacyclo-cumulenes, -pentynes, -pentadienes, -pentenes and -pentanes

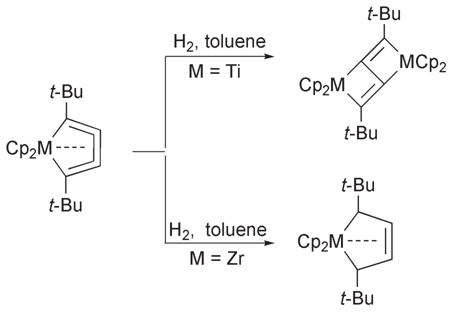
The symmetrically substituted five-membered metallacycles of titanium and zirconium possess different degrees of saturation of the molecules having three double, one triple, two double, one double or no unsaturated bond at all in the metallacycle. Their structural connection should allow the easy conversion from one type into another by hydrogenation. Starting from the metallacyclopentynes an exothermic course of the hydrogenation reaction was calculated (Scheme 22; A → B: -24.7 kcal mol^{-1}, B → C: -13.1 kcal mol^{-1}).[21]

First practical experiments[30] suggest that the realisation of this idea should indeed be possible but also indicate a strong influence of the different Cp′ ligands and the attached substituents. The 1-zirconacyclopent-3-yne *rac*-(ebthi)Zr(η^4-$H_2C_4H_2$) also was hydrogenated, but no products could be identified. Nevertheless the hydrogenation of other metallacyclocumulenes gave clear results (Scheme 23).

Whereas the titanacyclocumulene $Cp_2Ti(\eta^4$-*t*-BuC_4*t*-Bu) gave the dinuclear μ-"trans"-butadiyne complex, the corresponding zirconacyclocumulene $Cp_2Zr(\eta^4$-*t*-BuC_4*t*-Bu) yields the 1-zirconacyclopent-3-ene complex. The hydrogenation of the pentamethylcyclopentadienyl complexes $Cp^*_2Zr(\eta^4$-$RC_4R)$ did not stop at the metallacycle stage giving instead the dihydride and (depending on R) the fully hydrogenated Ph-$(CH_2)_4$-Ph (Scheme 22) or the partially hydrogenated Me_3Si-$CH{=}CH$-$(CH_2)_2$-$SiMe_3$. For R = Me also the $Cp^*_2ZrH_2$ was obtained but no defined organic products were isolated.



Scheme 22 Hydrogenation of five-membered metallacycles.



Scheme 23 Hydrogenation of metallacyclocumulenes.

Conclusion

Starting from metallacyclopropenes as three-membered ring systems of titanium and zirconium several symmetrically substituted five-membered metallacycles such as 1-metallacyclopentanes, 1-metallacyclopenta-2,4-dienes, 1-metallacyclopent-3-ynes and 1-metallacyclopenta-2,3,4-trienes (metallacyclocumulenes) were formed, showing a rich structural chemistry. The metallacyclopentynes and metallacyclocumulenes, often regarded as rather exotic, are very interesting classes of compounds especially from the theoretical and synthetical point of view, providing exciting new possibilities for future research: From the interpretation of the metallacyclopentynes as butatriene complexes, the isolobal 1-metalla-2,5-diheterocyclopent-3-ynes can be regarded as heterobutatriene complexes, playing an as yet unknown role in reductive C–C coupling reactions of carbon monoxide and isocyanides. The application and transfer of the chemical interaction between related classes of transition metal complexes following the isolobal concept gives a bright prospect for further applications of these early transition metal complexes to synthetic challenges.

Acknowledgements

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