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Highly strained metallacycles: synthesis, electronic nature and reactivity of group 4 1-metallacyclobuta-2,3-dienes

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Abstract

The content of this thesis is presented into three parts. The first part mainly focuses on expanding the scope of this class of group 4 1-metallacyclobuta-2,3-dienes. Two new phenyl-substituted dilithiated ligand precursors and four new 1-metallacyclobuta-2,3-dienes were synthesized and fully characterized. Solid state NMR and EPR spectroscopy, as well as cyclic voltammetry were used for the first time on these complexes to gain a better understanding of the nature of these complexes. The second part of this thesis focuses on synthesis, characterization and reactivity towards carbodiimides of a set of ring-strained group 4 *ansa*-metallocene-based 1-metallacyclobuta-2,3-dienes $Cp'_2M(Me_3SiC_3SiMe_3)$ (M = Ti, Zr; Cp' = indenyl or tetrahydroindenyl based *ansa*-Cp lignad). The reactions with carbodiimides (RN=C=NR) produced, depending on the substituents of the carbodiimide, either 2-aza-1-metallacyclobut-3-ene (R = *i*-Pr, Cy and *p*-Tol) or 2-aza-1-metallacychexa-2,4,5-triene complexes (R = $SiMe_3$). The third part explores the reactivity of 1-metallacyclobuta-2,3-dienes with diazenes. Depending on different metal centers, either N-N double bond cleavage occurs with Zr complexes, or diazene insertion into the Ti-C bond was observed when using Ti analogs.

Zusammenfassung

Diese Arbeit ist in drei Teile gegliedert. Der erste Teil dieser Arbeit konzentriert sich auf die Erweiterung dieser Klasse von Gruppe 4 1-Metallacyclobuta-2,3-dienen. Zwei neue phenylsubstituierte dilithiierte Ligandenvorstunfen und vier neue 1-Metallacyclobuta-2,3-diene wurden synthetisiert und vollständig charakterisiert. Festkörper-NMR- und EPR-Spektroskopie sowie Cyclovoltammetrie wurden zum ersten Mal auf diese Komplexe angewandt, um ein besseres Verständnis der Natur dieser Komplexe zu ermöglichen. Der zweite Teil konzentriert sich hauptsächlich auf die Synthese, Charakterisierung und Reakitivtät gegenüber Carbodiimiden einer Reihe von ringgespannten 1-Metallacyclobuta-2,3-dienen auf der Basis von *ansa* Gruppe 4 Metallocenen $Cp'_2M(Me_3SiC_3SiMe_3)$ (M = Ti, Zr; Cp' = Indenyl oder Tetrahydroindenyl auf der Basis von *ansa*-Cp lignad). Bei den Reaktionen mit Carbodiimiden (RN=C=NR) entstanden je nach Substituenten des Carbodiimids entweder 2-Aza-1-metallacyclobut-3-ene (R = *i*-Pr, Cy, und *p*-Tol) oder 2-Aza-1-metallacychexa-2,4,5-triene (R = $SiMe_3$). Im dritten Teil wird die Reaktivität von 1-Metallacyclobuta-2,3-dienen gegenüber Diazenen untersucht. Abhängig vom Metallzentrum wurde entweder eine N-N Doppelbindungsspaltung bei Verwendung von Zr als Metallzentrum oder eine Diazeninsertion in die Ti-C Bindung bei Verwendung von Ti als Metallzentrum beobachtet.

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List of Abbreviations

Ad	adamantyl
Å	Ångström
Ar	aryl
Bpin	pinacolborane
Bn	benzyl
n-Bu	*n*-butyl
t-Bu	*tert*-butyl
n-BuLi	n-Butyllithium
Cp	η^5-cyclopentadienyl
Cp*	η^5-1,2,3,4,5-pentamethylcyclopentadienyl
Cy	cyclohexyl
°C	degree Celsius
°	degree
C_6D_6	deuterated benzene
DCM	Dichloromethane
DFT	density function theory
dipp	2,6-diisopropylphenyl
dmap	4-Dimethylaminopyridine
dmp	2,6-Dimethylphenoxide
DME	dimethyl ether
e.g.	for example
Et	Ethyl
ebthi	η^5-ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)
eq.	equivalent
Hz	Hertz
p	*para*
rac	racemic mixture
XyNC	2,6-dimethylphenyl isocyanide
g	gramm
IR	Infrared Spectroscopy
L	ligand
[M]	metal
Me	methyl
Mes	mesityl
min	minute
mL	milliliter
meso	mesomerism
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy
NaHMDS	sodium bis(trimethylsilyl)amide
n-Pr	propyl
o	*ortho*
Ph	phenyl
ppm	parts per million
py	pyridine
i-Pr	isopropyl
PAHs	polycyclic aromatic hydrocarbons
rac	racemic
Tol	toluene
THF	tetrahydrofuran
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TM	transition metal
thi	η^5-tetrahydroindenyl
X	halide
δ	chemical shift

1 Introduction

Driven by today's urgent need for a sustainable, carbon-neutral society, researchers are investing a great deal of effort into developing more environmentally friendly methods and technologies in the chemical industry.[1] Catalysts offer an excellent opportunity to minimize energy consumption and waste generation in industrial production processes compared to the reactions using stoichiometric reagents.[2] Understanding reaction mechanisms and the catalytic process is an important step in designing more efficient catalysts. The metallacycles of group 4 metals, particularly of titanium and zirconium, have proved to be very important key intermediates and can be used as model compounds for highly reactive catalytically relevant species in a number of catalytic processes. Their in-depth studies have led to a detailed understanding of catalytic cycles, confirmed their mechanism and allowed the identification of important catalytic intermediates, e.g. in the metallocene-based Ziegler-Natta olefin polymerization reaction, which is being improved with increasing efficiency.[3]

The *all*-carbon strained metallacycles are derivatives of carbocyclic compounds in which a metal atom replaces at least one carbon atom (i.e., isoelectronic exchange of hydrocarbon fragments by [M:], which are carbene analogues) with a high degree of unsaturation or small ring size. Incorporation of unsaturation into smaller cyclic structures leads to an increase in ring strain. These complexes are often believed to violate the norm and are considered unstable. However, by choosing the right metal center and through control of the substituents, organometallic chemists have consistently synthesized those metallacycles of varying ring sizes and with a high degree of unsaturation since last century. Examples include metalla-cyclopropenes,[4] -cycloallenes,[5] -cyclocumulenes[6] and -cycloalkynes,[7] (or, according to the ring size, they can be divided into 3-, 4-, 5-, and 7-membered metallacycles) (**Figure 1**). This synthetic diversity provides an opportunity to understand the stoichiometric and catalytic reactions of organometallic compounds, at same time they also contribute significantly to our understanding of their reactivity and catalytic potential in the field of organometallic chemistry.

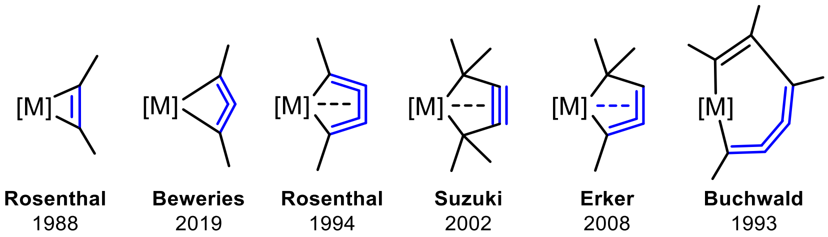


Figure 1. Examples for metalla-cyclopropenes, -cycloaallenes, -cyclocumulenes and -cycloalkynes with different ring size.

1.1 Three-membered metallacycles

Research focusing on the chemistry of group 4 three-membered metallacycles of titanium and zirconium began at about same time in the 1980s in different research groups. In 1980, Richard Threlkel, a PhD student in the Bercaw group at California Institute of Technology reported in his PhD thesis[8] a series of complexes of the type $Cp_2{*}M(RC_2R)$ (M = Ti, Zr, R = Me, Ph, Cp* = η^5-pentamethylcyclopentadienyl; **1-R** and **2**, **Figure 2**) synthesized from dinitrogen complexes $(Cp{*}_2Ti)_2N_2$ or $(Cp{*}_2ZrN_2)_2N_2$ and characterized by NMR, IR, elemental analysis, and mass spectrometry. He described these complexes as a monomeric monoacetylene complexes. By observing the reactions of $Cp{*}_2Ti(PhC_2Ph)$ (**1-Ph**) with H_2, he conjectured the dissociation of alkyne and the formation of highly reactive $[Cp{*}_2Ti]$ species.

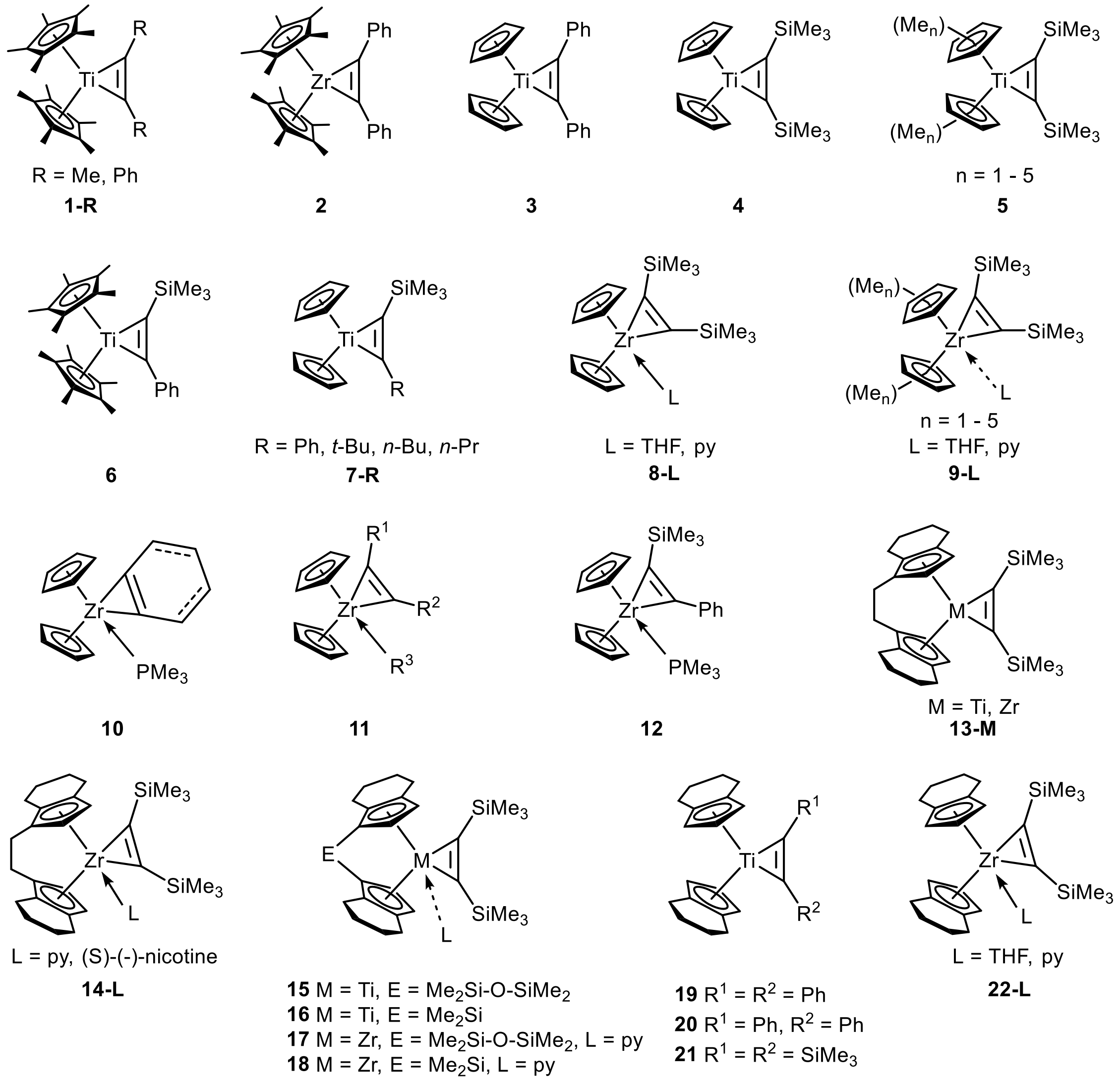
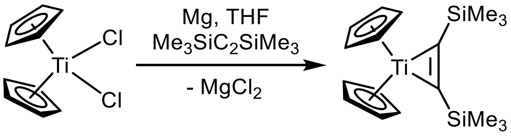


Figure 2. Overview of most kinds of three-membered metallacycles.

Later, the Vol'pin group in Moscow did a lot of work in titanocene three-membered metallacycles chemistry, which was inextricably linked to their background in organosilicon chemistry.[9] After several unsuccessful attempts, in 1982, Vladimir V. Burlakov from Vol'pin's group isolated the complex $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$ (**3**) in analytically pure state, but the crystals suitable for single crystal X-ray analysis could not be obtained. Later in 1985, Bercaw and co-workers briefly mentioned the complexes $Cp^*_2Ti(\eta^2\text{-}PhC_2Ph)$ and $Cp^*_2Ti(\eta^2\text{-}MeC_2Me)$ (**1-R**),[10] but unfortunately, also without single crystal X-ray structure. In 1988, Uwe Rosenthal joined Vol'pin's group as a postdoctoral associate, and with the knowledge of the successful synthesis of a nickel(0) complex with bis(trimethylsilyl)acetylene, $(Ph_3P)_2Ni(\eta^2\text{-}Me_3SiC_2SiMe_3)$,[11] he then proposed bis(trimethylsilyl)acetylene as the ideal candidate to prepare the stable, additional ligand free titanocene-alkyne complex $Cp_2Ti(\eta^2\text{-}RC_2R)$. In the same year, they reported the first $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ complex (**4**) as a golden yellow solid by reduction of Cp_2TiCl_2 with magnesium in the presence of bis(trimethylsilyl)acetylene in THF at room temperature (**Figure 3**).[12] Since then, using the same method, a number of titanium complexes of the type $Cp'_2Ti(\eta^2\text{-}Me_3SiC_2R)$ were prepared, e.g. Cp' = Cp*, R = Me_3Si (**5**)[13], Ph (**6**)[14] Cp' = Cp, R = Ph (**7-Ph**), as well as Cp' = Cp, R = *t*-Bu, *n*-Bu, *n*-Pr. (**7-R**).[15] Later, a complete series of the $(C_5H_{5\text{-}n}Me_n)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**5**) complexes has been obtained by Mach and co-workers.[16]



4

Figure 3. Synthesis of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$.

In case of zirconium, the first zirconocene alkyne complexes were reported by Buchwald and Takahashi independently in 1986. These zirconocene-alkyne complexes were obtained only with additionally coordinated electron donating ligands, e.g., PMe_3 or $PMePh_2$. Well-defined zirconocene alkyne complexes of the type $Cp_2Z(PMeR_2)$(acetylene) were obtained for the cyclic acetylenes benzyne[17,19] and cyclohexyne [18,19] (**10**), as well as for linear acetylenes $R^1C_2R^2$ where R^1 = H, R^2 = *n*-Bu[20] and $R^1 = R^2$ = Ph (**11**).[21] These complexes were generally synthesized from Cp_2ZrClH (Schwartz reagent) according to **Figure 4**[17,18,19,20] or from $Cp_2Zr(PMe_3)_2$ or $Cp_2Zr(PMe_3)(\eta^2\text{-olefin})$ complexes by adding the corresponding substituted alkyne.[21]

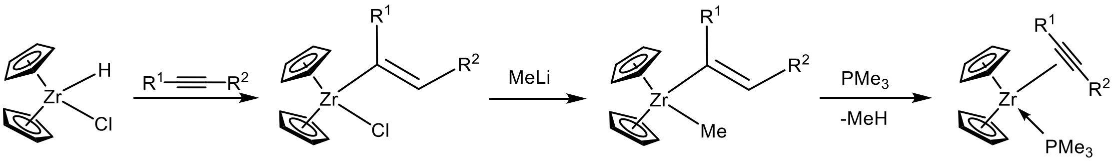


Figure 4. Synthesis of $Cp_2Zr(PMe_3)(\eta^2\text{-}RC_2R)$ starting from Cp_2ZrClH.

Later in 1991, Erker and Zwettler use a zirconacyclopentadiene complex and reacted it with a tenfold excess of trimethylphosphine at 70 °C, observing the liberation of one equivalent of phenyltrimethylsilylacetylene and the formation of $Cp_2Zr(PMe_3)(\eta^2\text{-}Me_3SiC_2Ph)$ (**12**, **Figure 5**).[22] Then they found the complex **12** loses its alkyne ligand and forms another very reactive species, which is believed to be [Cp_2Zr].

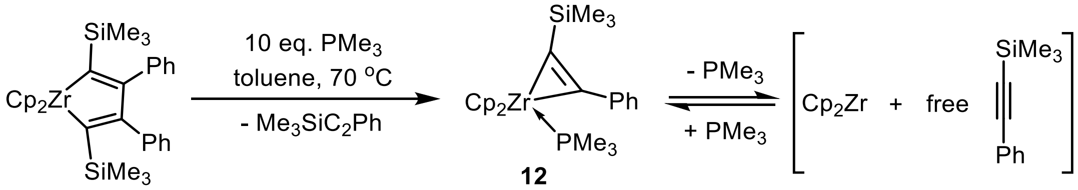


Figure 5. Synthesis of $Cp_2Zr(PMe_3)(\eta^2\text{-}SiMe_3C_2Ph)$.

Inspired by the successful synthesis of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**), in 1993 Rosenthal and co-workers followed the same reaction route, using magnesium as reduction reagent and bis(trimethylsilyl)acetylene as stabilizing ligand, successfully synthesized and isolated the first phosphine ligand free zirconium complex $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-THF, Figure 6**).[23] Different from the previous examples, zirconium complex **8** does not coordinate to any phosphine ligand, but to a THF molecule. The interaction between zirconium and THF was described as a weak interaction based on NMR spectroscopy, where only one NMR signal of both $SiMe_3$ groups and the Cp ligands could be observed in ^1H and ^{13}C NMR spectroscopy. This apparent equivalence of the two halves of the alkyne in solution can be explained by a fast exchange of free and coordinated THF molecules. However, when dissolved in hydrocarbon solvents like benzene, pentane or hexane, or exposure to high vacuum environment, decoordination of THF will occur, leading to a follow up Cp ring C-H activation reaction and formation of the dinuclear σ-alkenyl complex **23** (**Figure 6**).

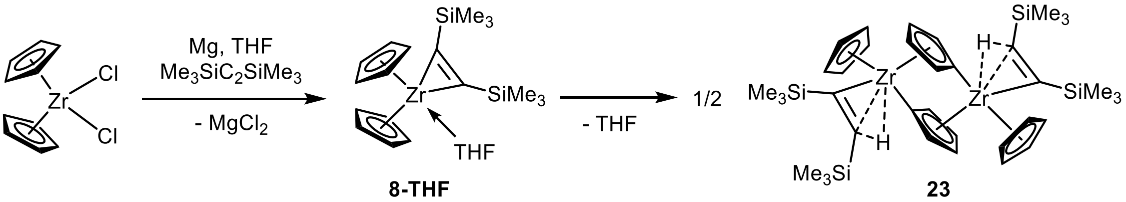


Figure 6. Synthesis of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and dimerization upon loss of coordinated THF.

This can be avoided by addition of pyridine into the system, resulting in a simple THF – pyridine exchange, yielding a more stable complex $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-py**).[24] This pyridine-stabilized complex can further exchange the stabilizing ligand with N-methyl-ε-caprolactam, forming a Cp_2Zr(N-Me-ε-caprolactam)(η^2-$Me_3SiC_2SiMe_3$) complex.[25] When treating complex **8-L** with acetone, the $Cp_2Zr(acetone)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ existed only in an equilibrium with its metallacyclic isomer, a zirconadihydrofuran complex (**24**, Figure 7).[26]

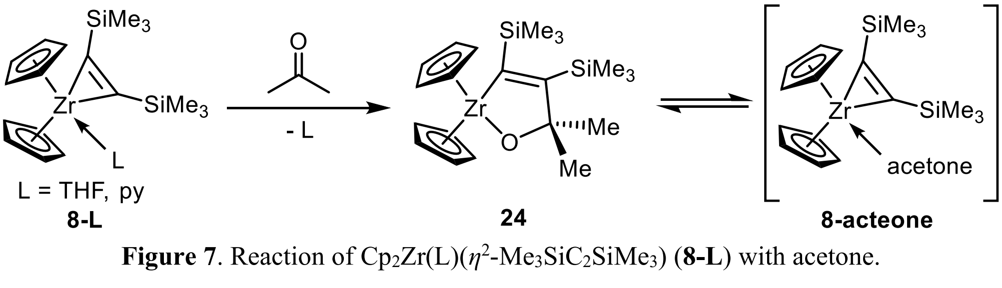


Figure 7. Reaction of $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-L**) with acetone.

According to later studies, this weak coordination of the solvent molecule can be modulated by the steric profile of the Cp ligands. For example, in the complexes $(C_5H_{5-n}Me_n)_2Zr(\eta^2-Me_3SiC_2SiMe_3)$ reported by Mach and co-workers,[27] when n = 3, 4 or 5, the THF solvent molecule will not coordinate to the zirconium anymore. For n = 2, the coordinated THF can be removed by high vacuum, indicated by a color change of the complex from honey-yellow to turquoise, but will not lead to its dimerization. Also, when using geometrically constrained ligand such as chiral *ansa*-metallocene, *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (*rac*-(ebthi) = *rac*-ethylenebis-(4,5,6,7-tetrahydro-1-indenyl), **13-Zr**, **Figure 2**) stable complexes can be isolated without any additional stabilizing ligand. In this case, pyridine or (*S*)-(-)-nicotine can be added as the stabilizing ligand (**14-L**, **Figure 2**).[28] As the chiral group 4 *ansa*-metallocene complexes are important in stereoselective synthesis and enantioselective reactions, Peulecke and Rosenthal then synthesized a series of group 4 *ansa*-metallocene alkyne complexes **15**, **17** and **18** (**Figure 2**).[29] Later in 1998, Rosenthal and co-workers investigated the influence of metals, alkyne substituents, Cp substitution and additional ligands on the stability of bridged and unbridged η^2-alkyne titanocene and zirconocene complexes.[30] The reduction of complex $MeSi_2(C_5H_4)TiCl_2$ with magnesium in the presence of PhC_2Ph in THF at room temperature does not give the expected titanocene complex $MeSi_2(C_5H_4)Ti(\eta^2-PhC_2Ph)$, instead, the corresponding five-membered ring complex $MeSi_2(C_5H_4)Ti(\eta^2-C_4Ph_4)$ was obtained. This coupling reaction is commonly observed for coordinatively and electronically unsaturated tolane complexes like $Cp_2Ti(\eta^2-PhC_2Ph)$ (**3**).[31] By using bis(trimethylsilyl)acetylene, the complex $MeSi_2(C_5H_4)Ti(\eta^2-MeSi_3C_2SiMe_3)$ **16** can be isolated. When using the unbridged complex $(thi)_2TiCl_2$ (thi = η^5-tetrahydroindenyl) as starting material in the reaction with different alkyne ligands, complexes **19**, **20** and **21** can be obtained. In case of zirconocene, the $(thi)_2Zr(L)(\eta^2-MeSi_3C_2SiMe_3)$ complexes with additional stabilizing ligand THF (**22-THF**) or pyridine (**22-py**) can be obtained. A reversible THF elimination was found in complex **22-THF** when increasing the temperature to the give green complex without THF coordination, which was confirmed by NMR spectroscopy at variable temperature.

As the scope of these titanocene- and zirconocene-alkyne complexes expanded, their reactivity was gradually discovered and further studied by researchers. There are two general possibilities of the reactivity: when considering these metallocene-alkyne complexes as metallacyclopropenes (with the metal in the +4 oxidation state), the insertion of substrate into the metal carbon bond of the metallacyclopropene ring (path I in **Figure 8**) is more likely to happen, and could be followed by cycloreversion and elimination of alkyne. In contrast, when considering it as acetylene π-complexes (with the metal in the +2 oxidation state), the dissociation of the alkyne with formation of a reactive 14 valence electron metallocene fragment [$Cp_2M(II)$] could occur (path II in **Figure 8**). This specie is subsequently trapped by reaction with substrates.

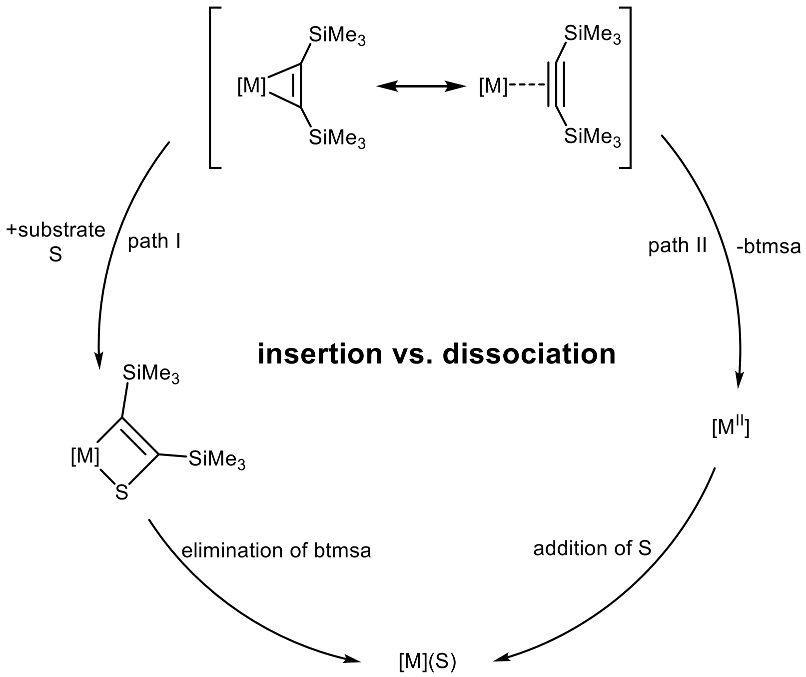
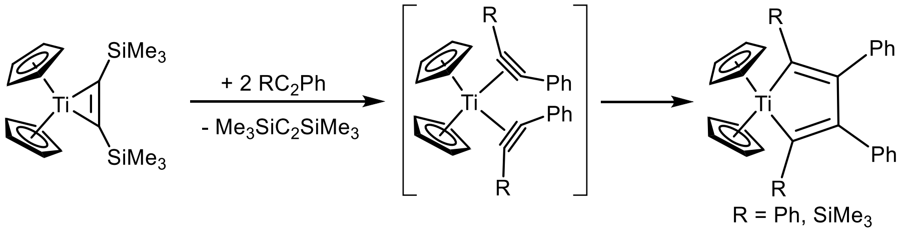


Figure 8. Insertion vs. dissociation reactivity of metallocene alkyne complexes.

During a series of reactivity investigations of titanocene- and zirconocene-alkyne complexes, the alkyne was believed as an excellent placeholder ligand which sufficiently stabilizes the metallocene fragment and which can be released quantitatively under mild conditions to generate the unstable and highly reactive 14 valence electron [Ti(II)] or [Zr(II)] source. These reactions are often influenced by the steric properties of the substrate, the stoichiometry used, the solvents, and other reaction conditions. By using different substituted Cp ligands (Cp, Cp* and *rac*-(ebthi)), additional ligands L (THF and pyridine), and the metals (Ti and Zr) the different reactivity can be achieved.

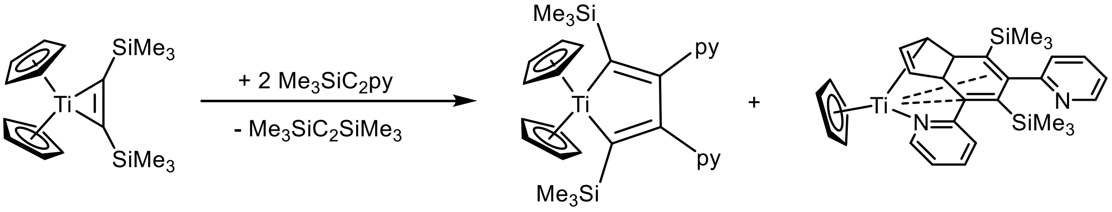
A wide variety of stoichiometric and catalytic reactions can be achieved by using this type of three-membered metallacycles. Here only some selected classic reactions are given as examples. Complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) can react with two equivalents of PhC_2Ph or PhC_2SiMe_3, producing the substituted titanacylopentadiene. With the unsymmetrically substituted PhC_2SiMe_3 the kinetically favored, unsymmetrically substituted titanacyclopentadiene was formed first which, after cycloreversion, gave the symmetrically substituted and thermodynamically more stable isomer (**Figure 9**).[14b] Due to steric reasons, the other symmetrical product with both Me_3Si groups in the 3,4-positions was not formed. Later, also the bis(trimethylstannyl)acetylene, $Me_3SnC{\equiv}CSnMe_3$, was shown to react with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) to give the complex $Cp^*_2Ti(\eta^2\text{-}Me_3SnC_2SnMe_3)$ by substitution of the alkyne.[32]



4 **25**

Figure 9. Reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with different substituted acetylenes.

The pyridyl-substituted acetylene Me_3SiC_2py reacts with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) and first forms the kinetically favored unsymmetrically substituted complex in addition to the symmetrically substituted thermodynamically more stable product (**26**, **Figure 10**). Upon standing in solution the unsymmetrically substituted complex will give an unusual coupling of one Cp ligand with the tetrasubstituted metallacyclopentadiene unit with formation of a dihydroindenyl complex (Cp activation product). Also, the symmetrical 3,4-$(Me_3Si)_2$ product was not formed.[33]



4 **26** "Cp activation product"

Figure 10. Reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with pyridyl-substituted acetylene.

Based on this alkyne exchange reactivity, several multifold coupling reactions of tris(diyne) and pentakis(diyne) substrates were realized by Tilley and coworkers by using $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-py**, **Figure 11**). With an excess of benzoic acid, the intermediate zirconacyclopentadiene complexes (**27** and **28**) produced the corresponding products of protodemetallation in high yields, which could be very difficult to obtain by using traditional synthesis methods, either requiring multiple, or only giving low yields.[34] This chemistry can thus have a huge potential for the construction of novel polycyclic aromatic hydrocarbons (PAHs), which have a great application prospects, e.g., in cathode materials for aluminum-ion batteries.

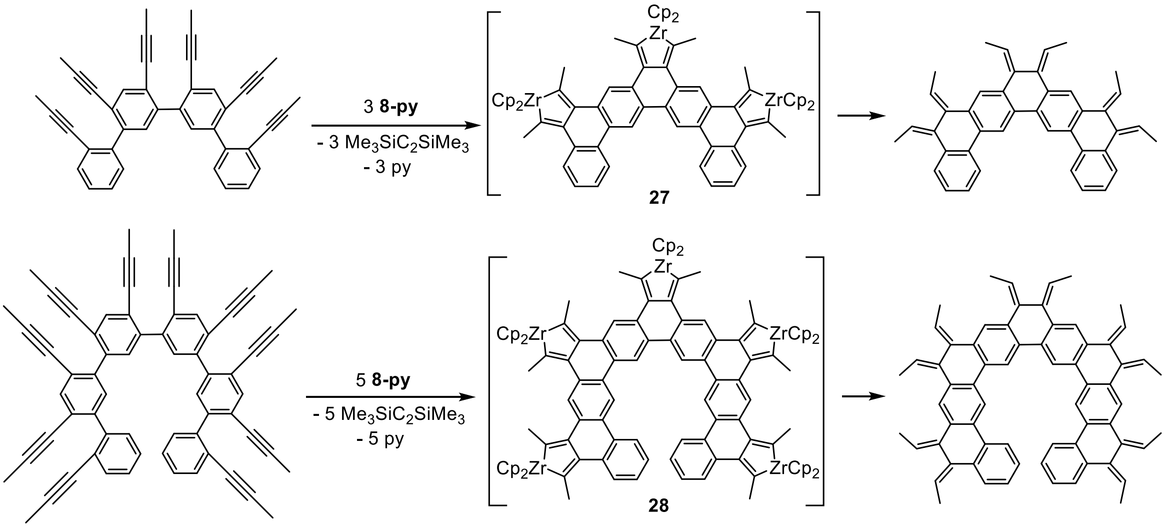


Figure 11. Examples of multifold couplings of tris- and pentakis(diynes) with $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ to PAHs and protodemetallation.

Staubitz and coworkers presented and compared intermolecular coupling reactions of several heterodisubstituted alkynes and octadiynes $RC\equiv C(CH_2)_4C\equiv CR$ (R = $SnMe_3$, Bpin, 4-thiophenyl, 2-methoxy, 2-bromo- and 2-iodo-4-thiophenyl etc.) to give zirconacyclopentadienes comparing Negishi's reagent and the Rosenthal's reagent $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-py**, **Figure 12**).[35] The result shows that **8-py** was much more efficient for the synthesis of zirconacyclopentadienes in most of the cases with respect to yield, stability of the zirconacyclopentadiene, and reaction time.

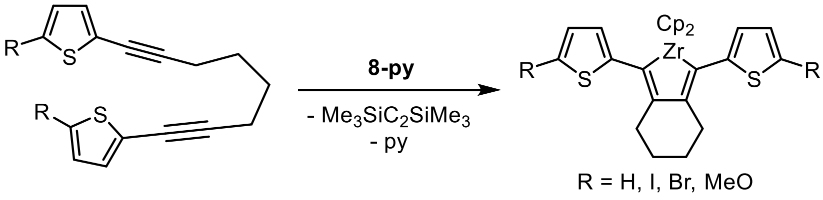


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Figure 12. Reactivity of $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with bis-substituted octadiynes and the formation of 1-zirconacyclopenta-2,4-dienes.

In the reaction of complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) with butadiynes RC≡C-C≡CR (R = Ph, *t*-Bu) in 2:1 ratio, formation of binuclear complexes **31** with intact C_4 units between the two titanium centers was observed.[36] The diynes were transformed to zigzag butadiene ligands between to metallocene cores. The five-membered titanacyclocumulenes (1-metallacyclopenta-2,3,4-trienes, $Cp_2Ti(\eta^4\text{-}RC{=}C{=}C{=}CR$, **30**) were formed with a ratio of 1:1 (**Figure 13**).[37] Such five-membered metallacyclocumulenes are very unusual, showing an almost planar arrangement of the metallacycle with three C-C double bonds (discussed in detail in section **1.2.2**).

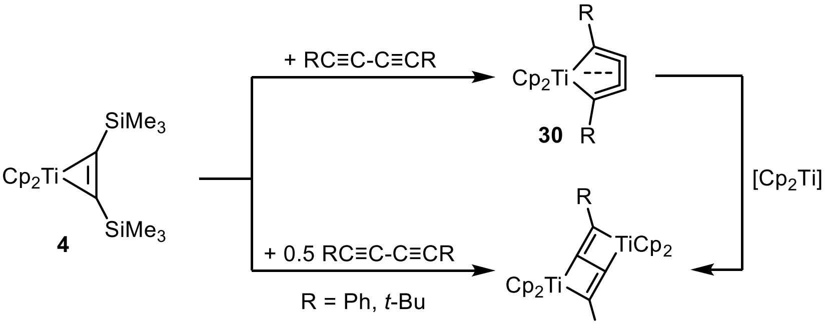


Figure 13. Complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ react with butadiynes.

Some nitrogen-containing compounds can also react with these three-membered metallacycles. Reaction of 1,4-diaza-1,3-dienes with titanocene- or zirconocene-alkyne complexes resulted in the formation of diazametallacylopentenes with the C-C double bond additionally coordinated to the metal center. In contrast, the reaction of titanocene complexes with 2,3-diaza-1,3-dienes showed a more diverse reactivity, giving diazametallacyclopentenes (**32**), bis(imide) complexes (**33**) or diazametallacyclopropanes (**34**) by N-N bond cleavage (**Figure 14**).[38]

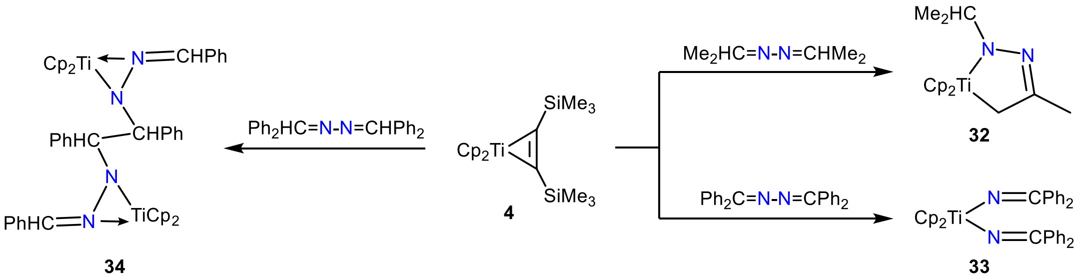
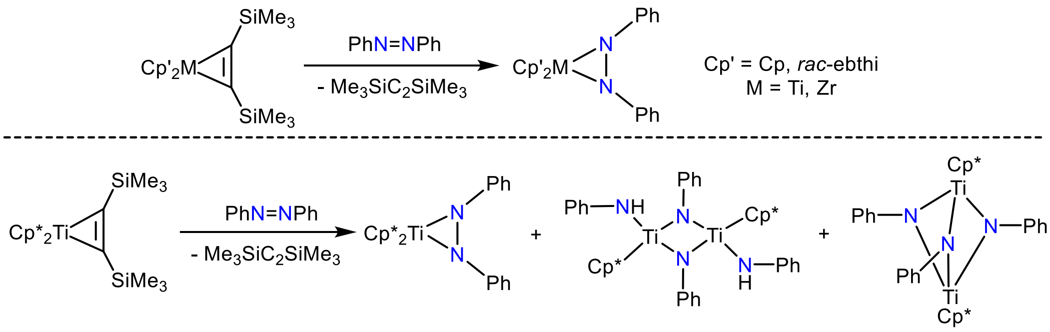


Figure 14. Reaction 1,4-diaza-1,3-dienes with titanocene or zirconocene alkyne complexes.

In 2010, Rosenthal and co-workers reported the reaction of alkyne complexes $Cp'_2(L)M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp’ = Cp, *rac*-ebthi; M = Ti, Zr; L = pyridine) with azobenzene to give the diazene complexes (**Figure 15**, top). Furthermore, three different products (**35 - 36**) could be isolated when using $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**5**, **Figure 2)** react with azobenzene (**Figure 15**, bottom).[39]



5 **35** **36** **37**

Figure 15. Reactions of $Cp'_2(L)M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with azobenzene. Top: ligand exchange reaction; bottom: ligand exchange and N-N bond cleavage.

A variety of products can be obtained by reacting $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) with different substituted carbodiimides (RN=C=NR; R = $SiMe_3$, Cy, *i*-Pr, *p*-Tol) depending on the used solvent, reaction temperature and times. A summary is presented in **Figure 16**.

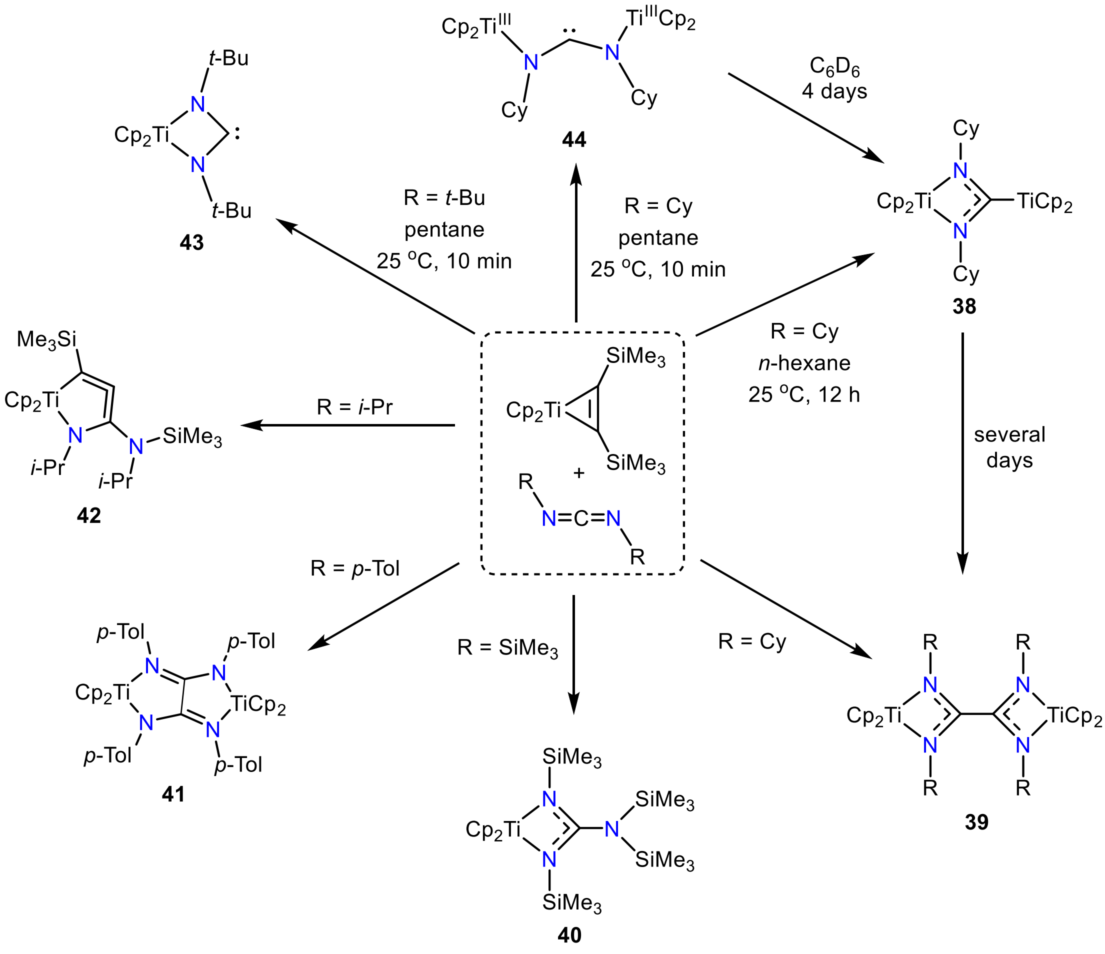


Figure 16. Summary of the reactions of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with carbodiimides.

The reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) with different carbodiimide substrates RN=C=NR' (R = *t*-Bu, R' = Et; R = R' = *i*-Pr, *t*-Bu, $SiMe_3$, 2,4,6-Me-C_6H_2, 2,6-*i*-Pr-C_6H_3) was investigated by Rosenthal and co-workers in 2012.[40] They found that the product complexes show dismantlement, isomerization or C-C coupling of the applied carbodiimide substrates, respectively, to form mono-, di- and tetranuclear titanium(III) complexes. By using the *N,N'*-diphenylformamidine in the reaction with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**), the formation of four-membered heterometallacyclic complex $Cp_2Ti(\kappa^2$-*N,N'*-PhN-C(H)-NPh) can be observed.[41] Both complexes $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) and $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-py**) react with carbodiimides RN=C=NR (R = Cy (**39**), *i*-Pr (**42**), *p*-Tol (**51**)), leading to the formation of five-membered hetero-metallacycloallenes.[42] Interestingly, when the complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) react with carbodiimides RN=C=NR at room temperature, instead of many different products observed earlier, Tonks and co-workers found the formation of an unusual four-membered metallacyle $Cp_2Ti(\kappa^2$-*C,C*-*t*-BuN=C=N*t*-Bu) (**43**), which is the first example of a complex with an κ^2coordination mode of a heterocumulene featuring a free carbene at the central C atom.[43]

Because of the diverse and extraordinary reactivity of these three-membered metallacycles, despite the important contributions from the past 35 years, these compounds offer a lot of potential for further applications. This includes the development of new synthesis methods of these type complexes as well as the new applications. From the very first Mg(0) reduction of Cp_2TiCl_2 in 1988, to using *n*-butyllithium to reduce Cp_2TiCl_2 in 1993,[44] to using Cp_2TiCl_2 in the reaction with $Me_2HSiC_2SiMe_2H$,[45] until recent work where Cp_2TiCl_2 react with EtMgBr in the presence of $Me_3SiC_2SiMe_3$,[46] the methods of preparing such complexes are also constantly improving, aiming obtain higher yields and more efficient operations. Future application of these complexes could include main group chemistry, where already now unusual new bonding modes and valence states of main group compounds are realized.[47]

1.2 Five-membered metallacycles

In addition to three-membered metallacycles, five-membered titana- and zirconacycles represent another important part in the chemistry of metallacycles. The types of symmetrically substituted five-membered metallacycles are summarized in **Figure 17**.

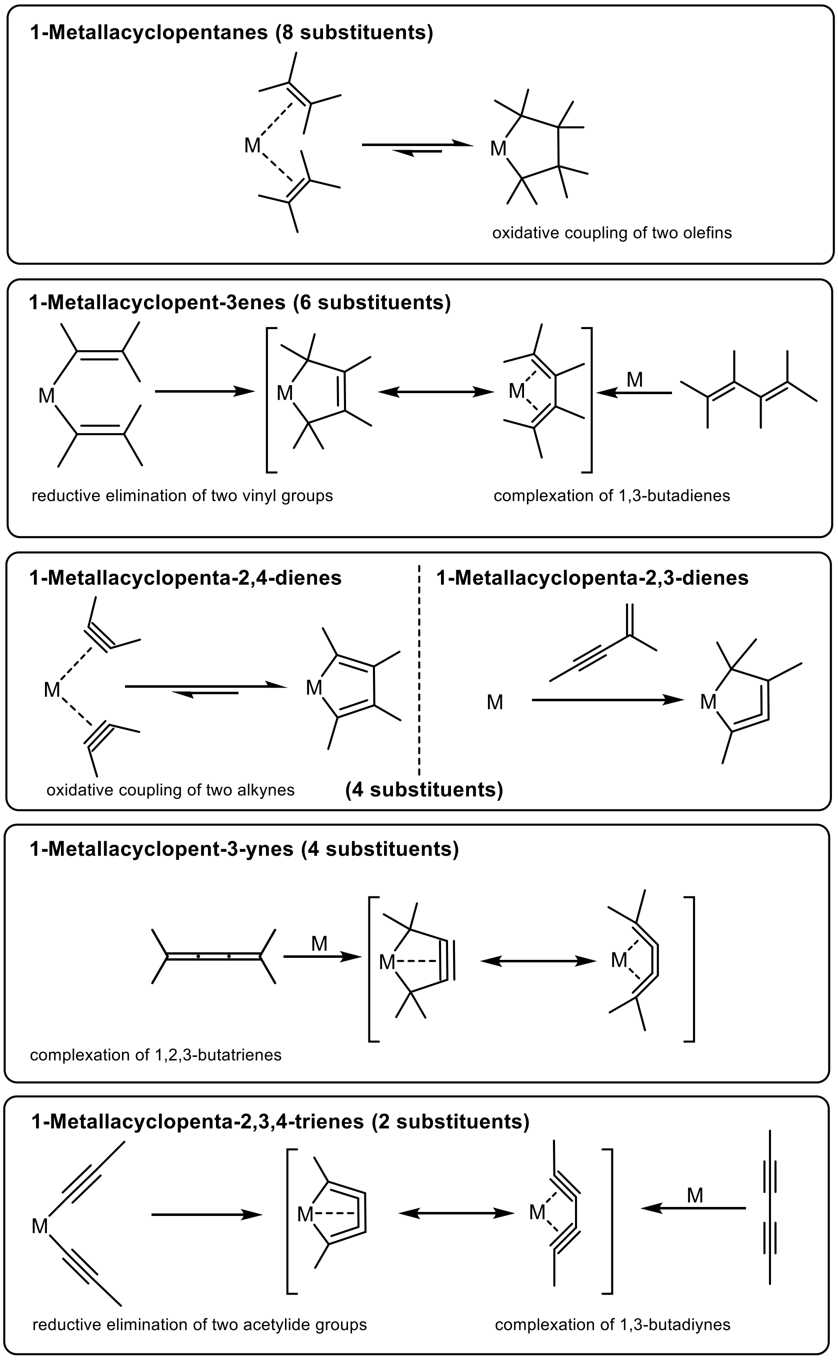


Figure 17. Formation of group 4 five-membered metallacycles (M = group 4 metal fragment).

1-metalla-cyclopentanes, -cyclopent-3-enes[48] and -cyclopenta-2,4-dienes[49] are well investigated and have found use in many important stoichiometric and catalytic reactions. These metallacycles possess more substituents and show a lower degree of saturation compared to 1-metallacycloallenes, 1-metallacyclopent-3-ynes and 1-metallacyclopenta-2,3,4-trienes, which also have much higher ring strain.

In this chapter, the synthesis of highly ring strained five-membered metallacycles, 1-metallacyclopent-3-ynes (chapter **1.2.1**), 1-metallacyclopenta-2,3,4-trienes (chapter **1.2.2**) and 1-metallacyclopenta-2,3-dienes (chapter **1.2.3**) as well as the progress of research on their reactivity will be discussed.

1.2.1 Synthesis and reactivity of 1-metallacyclopent-3-yne complexes

In 1996 Maercker and co-workers found the 1-titanacyclopent-3-yne as an intermediate in the reaction of the cumulene complex $Cp_2Ti(\eta^2\text{-}Me_2C{=}C{=}C{=}CMe_2)$ and $[Cp_2Ti]$.[50] The first 1-zirconacyclopent-3-ynes (**45**) were synthesized by Suzuki and co-workers in 2002. They used [Cp'$_2$Zr], generated using the Negishi method, and 1,4-disubstituted (*Z*)-butatrienes RHC=C=C=CHR (R = Me_3Si, *t*-Bu) as starting materials (**Figure 18**).[7a]

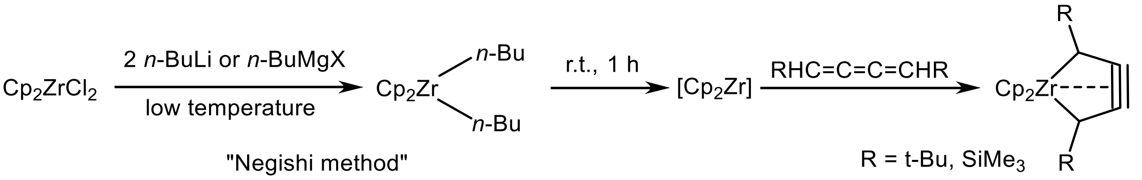


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Figure 18. Formation of 1-zirconacyclopent-3-ynes in the reaction of [Cp'$_2$Zr] with 1,4-disubstituted (*Z*)-butatrienes.

Later Suzuki and co-workers showed that 1-zirconacyclopent-3-ynes could be produced by the reaction of Cp_2ZrCl_2 and 1,4-dichlorobut-2-yne with Mg. They claimed this compound as first "unsubstituted" metallacyclopent-3-yne (**46**, **Figure 19**).[7b]

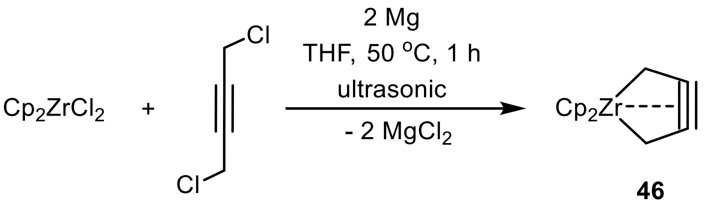

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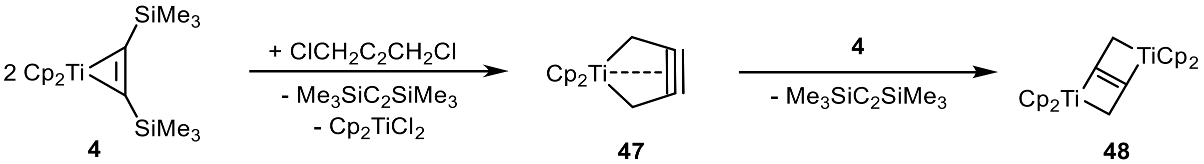
Figure 19. Formation of unsubstituted 1-metallacyclopent-3-yne in the reaction of Cp_2ZrCl_2 with 1,4-dichlorobut-2-yne.

The 1-titanacyclopent-3-yne (**47**) was obtained at the same time in the reaction of two equivalents of the Ti(II) source $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) 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 equivalent coordinates the butatriene, giving the unsaturated 1-titanacyclopent-3-yne. Complex **47** can react with another equivalent $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) to give 2,5-dititanabicyclo[2.2.0]hex-1(4)-ene (**48**, **Figure 20**).[51]



4 **47** **48**

Figure 20. Formation of 1-titanacyclopent-3-yne complex in the reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with 1,4-dichlorobut-3-yne.

In 2005, Rosenthal and co-workers reported that the metallacyclopent-3-ynes react with the Lewis acid $B(C_6F_5)_3$ under ring opening of the metallacycle and formation of the zwitterionic complexes (**49** and **50**, **Figure 21**). The corresponding Zr complexes are active single-component catalysts for ethylene polymerization.[52]

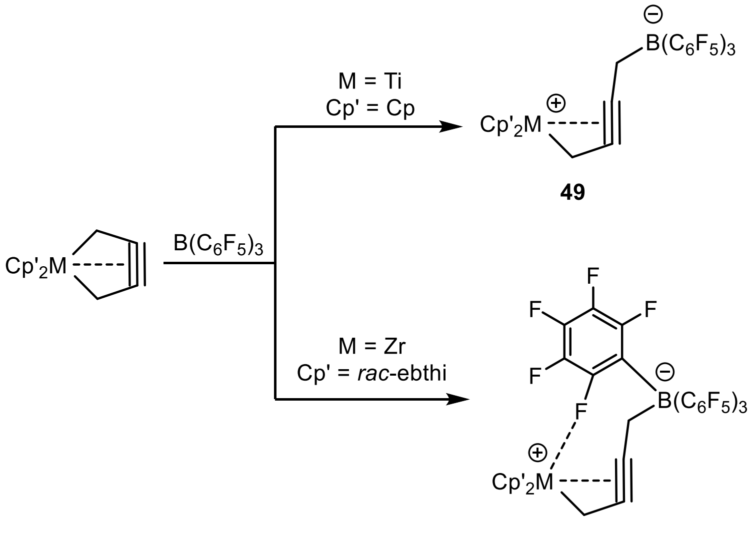


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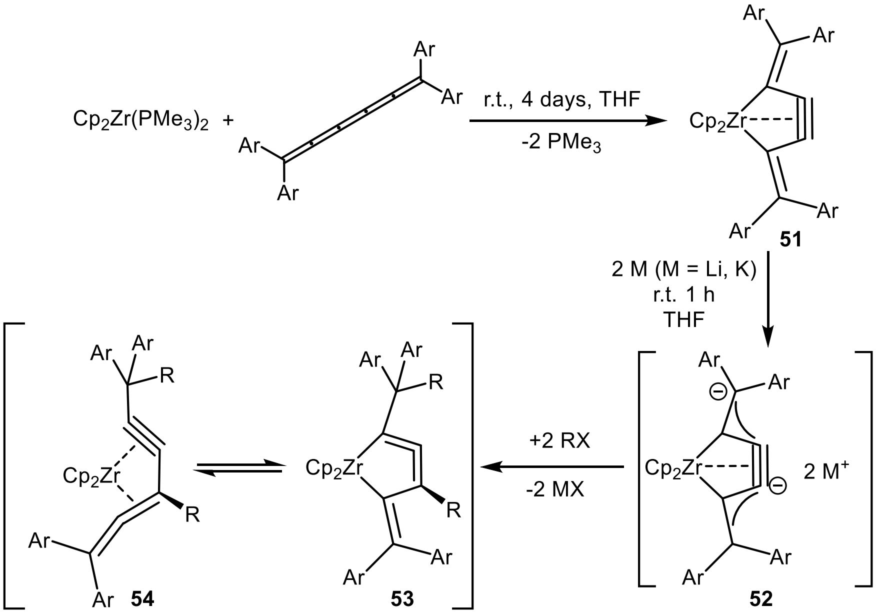
Figure 21. Reactions of 1-metallacyclopent-3-ynes with $B(C_5F_6)_3$.

In 2008, Suzuki and co-workers reported the synthesis of 1-zirconacyclopenta-2,3-dienes using a different method.[5b] By treating the Zr(II) source $Cp_2Zr(PMe_3)_2$ with 1,1,6,6-tetrakis(4-ethylphenyl)-1,2,3,4,5-hexapentaene, a 2,5-bisalkylidene-1-zirconacyclopent-3-yne (**51**) can be obtained. Then, this 1-zirconacyclopent-3-yne (**51**) can form a di-anionic species (**52**) when reacted with strong reducing agents such as lithium powder or potassium graphite. The subsequent protonation of this di-anionic species will then lead to the formation of 1-zirconacyclopent-3-ene (**53**) as main product and 1-zirconacyclopenta-2,3-diene (**54**) as minor part (**Figure 22**).



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54 **53** **52**

Figure 22. Formation of 1-zirconacyclopenta-2,3-dienes.

Because of the unique structure, the 1,3-butadiynes can react as bridging ligands. The 1-zirconacyclopent-3-yne forms a cycloalkyne complex (**55**) with "$Cp_2Zr(PMe_3)$", containing a C_4 unit between the metals, described as a 1-zirconacyclopent-3-yne $Cp_2Zr(\eta^4\text{-}H_2C_4H_2)$. The same reactivity is observed with late transition metal fragments such as with the nickel(0) complex $L_2Ni(\eta^2\text{-}C_2H_4)$ (L = PPh_3 or PCy_3) to give the analogous dinuclear complexes $Cp_2Zr[\mu\text{-}(\eta^4\text{-}H_2C_4H_2)]NiL_2$ (L = PPh_3 or PCy_3, **56**, **Figure 23**).[53] The formed 1-zirconacyclopent-3-ene unit in these complexes is not planar.

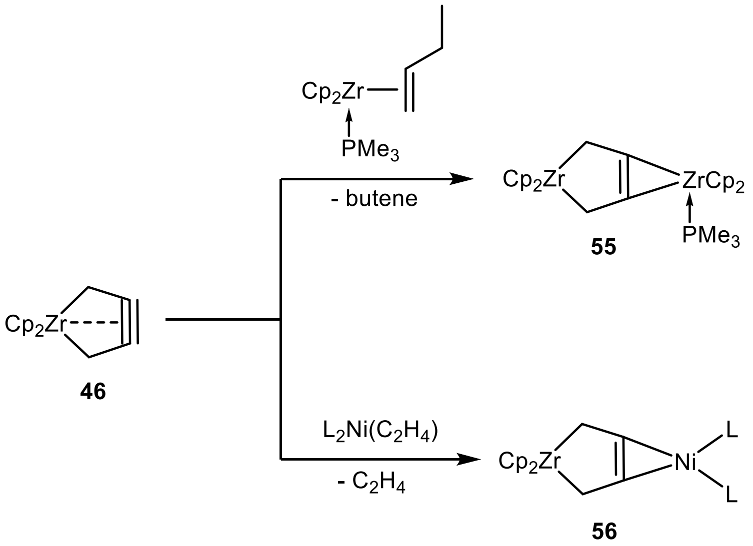
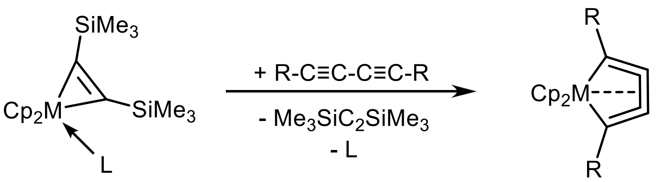


Figure 23. *Cis*-complexation of 1-zirconacyclopentynes to early and late transition metal fragments.

1.2.2 Synthesis and reactivity of 1-metallacyclopenta-2,3,4-triene complexes

As further examples for highly unsaturated metallacycles, 1-metallacyclopenta-2,3,4-triene complexes have also been well studied since the 1990s. The first stable 1-zirconacyclopenta-2,3,4-triene, $Cp_2Zr(\eta^4\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ (**58B**), was obtained from the reaction of $Cp_2Zr(pyridine)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**8-py**) with 1,3-butadiyne *t*-BuC≡C-C≡C-*t*-Bu.[6b] Later, the titanacyclocumulenes $Cp_2Ti(\eta^4\text{-}RC_4R)$ (**57A**, R = t-Bu, Ph) were also obtained by using a similar reaction procedure starting from $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**4**) and RC≡C-C≡CR (**Figure 24**).[6c]



57A M = Ti, R = *t*-Bu, Ph, L = -
58A M = Zr, R = *t*-Bu, L = pyridine

Figure 24. Formation of 1-metallacyclocumulenes in the reaction of $Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ complexes with 1,3-butadiyne.

Exposure of decamethylzirconocene bis(acetylide) complex $Cp^*_2Zr(\sigma\text{-}C{\equiv}CR)_2$ to sunlight resulted in C-C coupling of the alkynyl groups to give the 1-metallacyclopenta-2,3,4-triene complexes $Cp^*_2Zr(\eta^4\text{-}RC_4R)$ (R = Ph, $SiMe_3$, Me) in high yields.[54] The reduction of $Cp^*_2ZrCl_2$ with magnesium in the presence of the hexatriyne *t*-Bu-C≡C-C≡C-C≡C-*t*-Bu yielded the unsymmetrically substituted

$Cp^*_2Zr(\eta^4$-*t*-Bu-C_4-C≡C-*t*-Bu) (**58B**). In contrast, with $Cp^*_2TiCl_2$ the titanacyclopropene $Cp_2Ti(\eta^2$-*t*-Bu-C≡CC_2C≡C-*t*-Bu) (**57B**), containing two alkynyl substituents was obtained (**Figure 25**).[55]

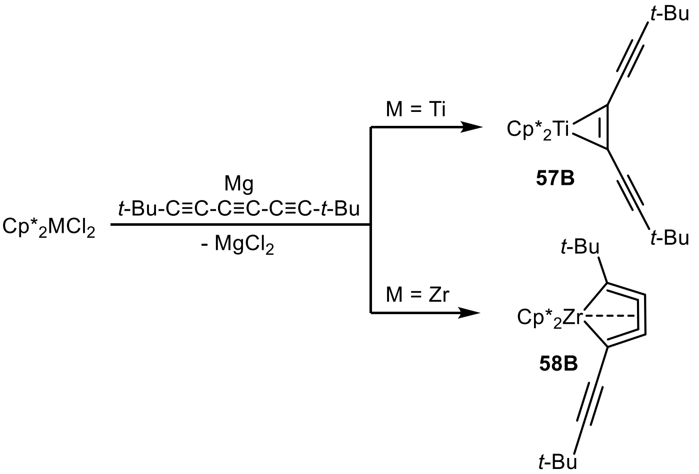


Figure 25. Reductions of $Cp^*_2MCl_2$ in the presence of hexatriynes.

The interaction of a free, non-coordinated triple bond of polyyne systems with the larger metal center zirconium may lead to the observed three- or five-membered metallacycles, or an equilibrium between η^2- and η^4 coordination. This can be assigned as "sliding" behavior for Cp^*_2Zr type complexes (**Figure 26**).

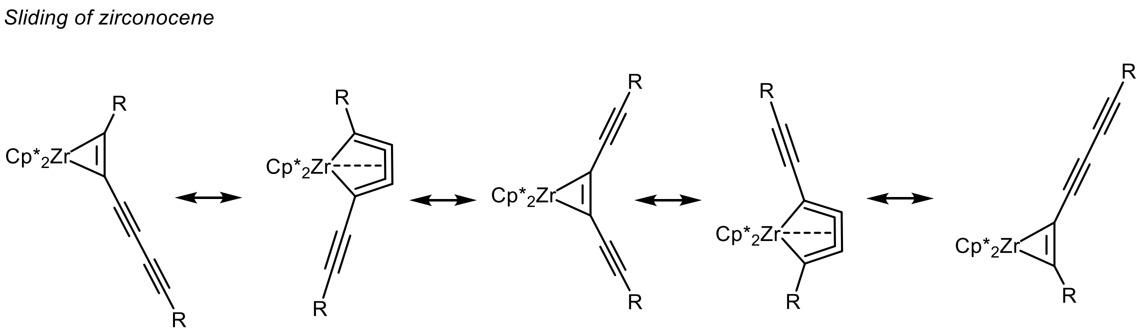

Sliding of zirconocene

Figure 26. Sliding of a zirconocene along the backbone of a triyne

The mesomerism of metallacycles and π-complex and the equilibrium between η^2- and η^4-coordination make things more difficult to understand. Both components of the equilibrium mixture can react with each other to afford an unsymmetric complex in which a titanacyclopentadiene is anellated to a titanacyclopentene (**59** and **60**, **Figure 27**), and the influences of Cp ligands and the metal center also leads to a reactivity difference for these systems. The real bonding situation in metallacyclopentynes and metallacyclocumulenes with its consequences for their reactivity still needs further, more systematic, investigation.

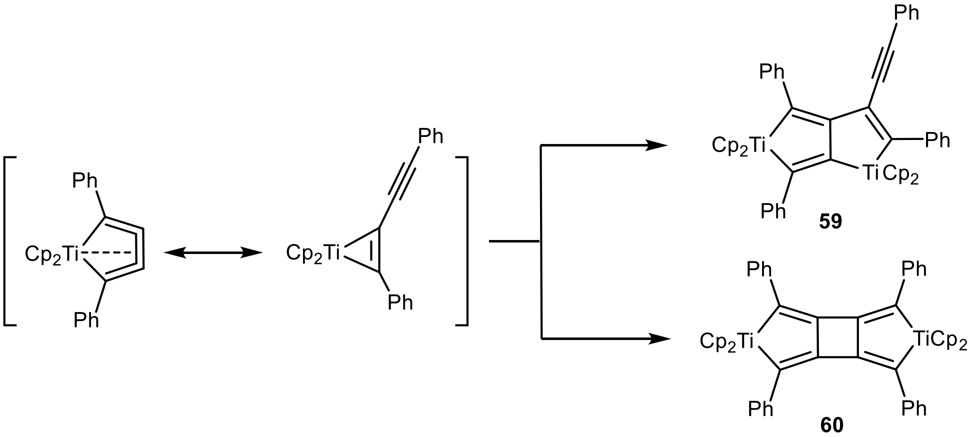
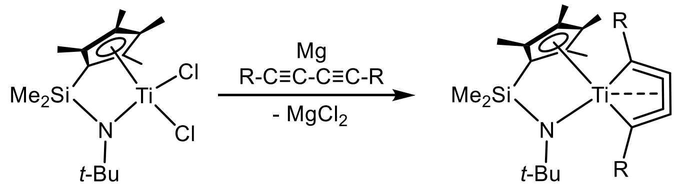


Figure 27. Coupling of 1-metallacyclocumulene.

Besides the Cp ligands, there are also some examples of half-sandwich or non-metallocene metallacyclocumulenes. For example, the first half-sandwich titanacyclocumulene complexes containing linked amido-cyclopentadienyl ligands, $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N\text{-}t\text{-}Bu)Ti(\eta^4\text{-}RC_4R)$ (**61**, R = *t*-Bu, $SiMe_3$), were prepared by reaction of the dichloride complex $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N\text{-}t\text{-}Bu)TiCl_2$ with magnesium in the presence of disubstituted 1,3-butadiynes (**Figure 28**).[56]



61 R = *t*-Bu, $SiMe_3$

Figure 28. Formation of half-sandwich metallacyclocumulenes.

Ashe and co-workers reported the formation of a set of zirconacyclocumulenes of the type $(\eta^6\text{-}C_5H_5BX)_2Zr(\eta^4\text{-}RC_4R)$ (**62**, X = *i*-Pr_2N, R = Ph; X = Ph, R = Ph; X = Ph, R = Et) by using bis(1-boratabenzene)bis(trimethylphosphine)zirconium(II) complexes, reacted with 1,3-diynes RC≡C-C≡CR (**Figure 29**).[57]

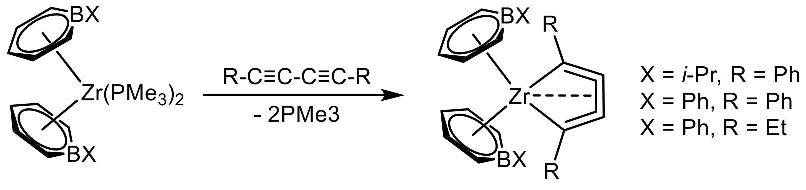


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Figure 29. Formation of non-metallocene-based 1-metallacyclocumulenes.

A theoretical study by Jemmis and Giju showed that titana- and zircona-cyclocumulenes are thermodynamically more stable compared to the isomeric bis σ-acetylide complexes.[58] 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. For Ti and Zr the central double bond is intact and there is no d-π^* back-bonding for the formal oxidation state +4, with a d^0 electron count. In contrast, for late transition metal complexes such as 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 central C-C bond.[59] Other studies of the energetics of the metal-free organic structure cyclopentyne and its organometallic analogs obtained by replacing the CH_2 groups by the metallocene [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. Lin and co-workers suggested that the zirconocene complex is better described by resonance hybrids involving a metallacyclopentyne and a butatriene complex Lewis structure.[60]

The zirconacyclocumulene $Cp^*_2Zr(\eta^4\text{-}Me_3SiC_4SiMe_3)$ reacted with two equivalents of carbon dioxide to form a cumulenic dicarboxylate complex (**63**) by a formal twofold insertion into M-C bond of the η^4-complex (**Figure 30**).[54]

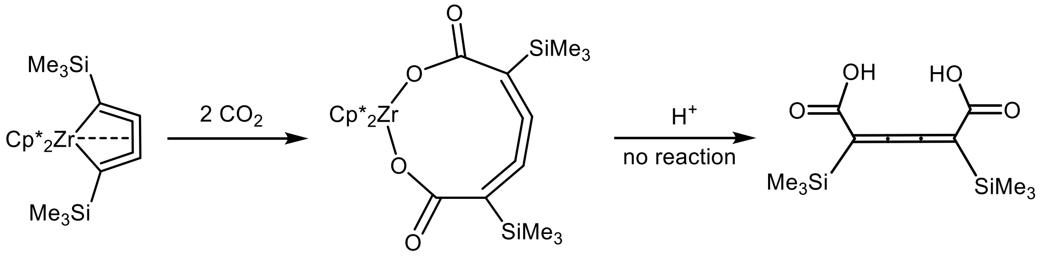

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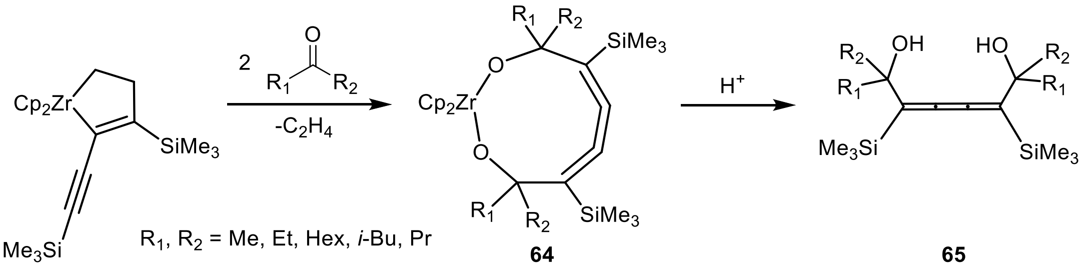
Figure 30. Carbon dioxide insertions into a 1-zirconacyuclocumulene.

It is not clear whether the zirconacyclocumulene reacts as an η^2 or η^4-complex. Acidolysis of the insertion product did not yield the corresponding [3]cumulenic dicarboxylic acid or ester. Liu and co-workers described an elegant route to *cis*-[3]cumulenic diols (**65**) by the reaction of alkynylated zirconacyclopentenes with ketones for which zirconacyclocumulenes (**64**) were assumed as intermediates, formed by extrusion of ethylene (**Figure 31**).[61] This reaction is related to the carbon dioxide insertion mentioned above.



64

65

Figure 31. Formal twofold ketone insertion into a 1-zirconacyclocumulene.

Metallacyclocumulenes are discussed as key-intermediates in the coupling and cleavage of 1,3-butadiynes. These metallacycles 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 (**Figure 32**). There is only a very small number of examples for the coupling of vinylidene ligands to butatrienes, which normally should be observed.

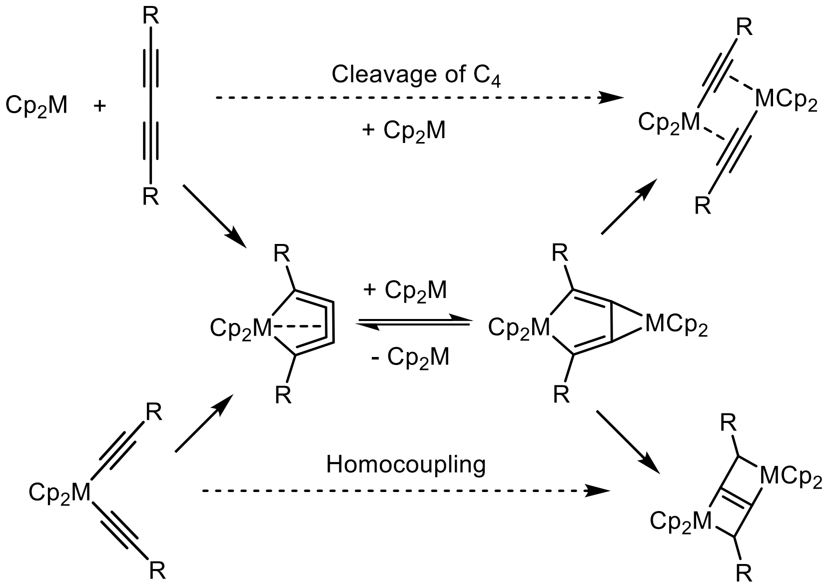
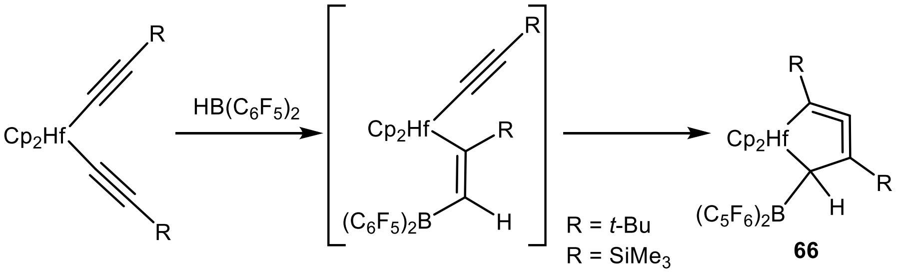


Figure 32. 1-Metallacycumulenes as key intermediates in cleavage and coupling reactions.

1.2.3 Synthesis and reactivity of 1-metallacyclopenta-2,3-diene complexes

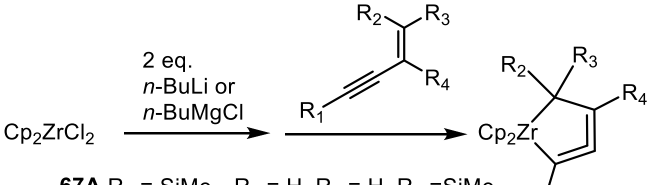
The existence of 1-metallacyclopenta-2,3-diene complexes was initially predicted by Rosenthal in 2004.[62] The first examples were successfully synthesized and isolated later by Erker[63], Suzuki[64] and co-workers, respectively. Compared to 1-metallacyclopent-3-ynes and 1-metallacyclopenta-2,3,4-trienes, 1-metallacyclopenta-2,3-dienes have a lower degree of unsaturation, but the allene feature imposes a higher ring strain of the metallacyclic unit than in 1-metalla-cyclopentanes, -cyclopent-3-enes and -cyclopenta-2,4-dienes.



66

Figure 33. Formation of 1-hafnacyclopenta-2,3-dienes.

When treating $Cp_2Hf(C{\equiv}CR)_2$ (R = $SiMe_3$, *t*-Bu) with $HB(C_5F_6)_2$, Erker and co-workers found the subsequent C-H and C-Hf σ-bond formation to give a reactive intermediate, which finally leads to the formation of 1-metallacyclopenta-2,3-dienes (**Figure 33**). Over the next few years, Erker[65] and Suzuki[66] reported a series of 1-zirconacyclopenta-2,3-dienes by using low oxidation state metal complexes in reactions with R_1-C≡C-C(R_4)=C(R_2R_3). The selected results are summarized in **Figure 34**.



67A R_1 = $SiMe_3$, R_2 = H, R_3 = H, R_4 =$SiMe_3$
67B R_1 = *t*-Bu, R_2 = H, R_3 = H, R_4 = Me
67C R_1 = *t*-Bu, R_2 = H, R_3 = Ph, R_4 = H
67D R_1 = $SiMe_3$, R_2 = H, R_3 = $SiMe_3$, R_4 = H

Figure 34. Formation of 1-zirconacyclopenta-2,3-dienes.

The reactivity of 1-zirconacyclopenta-2,3-dienes with many different substrates like ketones, nitriles, esters, diethyl carbonate and isocyanates were mainly investigated by Suzuki and co-workers.[67]

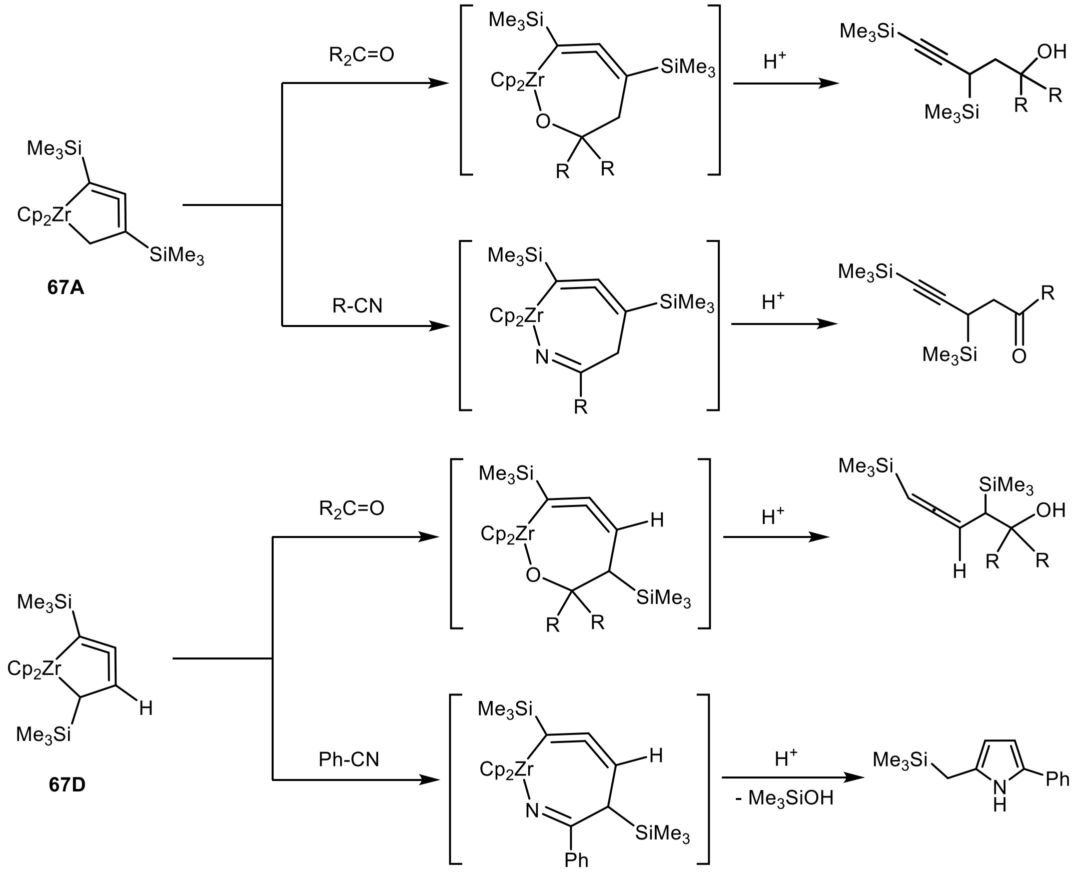


Figure 35. Reaction of 2,4- and 2,5-substituted 1-zirconacyclopent-2,3-dienes with ketones and nitriles.

The reactions of 2,4-substituted 1-zirconacyclopent-2,3-dienes (**67A**) with ketones yield, after hydrolysis, alkynyl alcohols (**Figure 35**). For the reactions of 2,5-bis(trialkylsilyl)compounds (**67D**) with ketones, allenyl alcohols were formed. In the reactions with a nitrile, via seven-membered 1-aza-2-zirconacyclopenta-3,4,7-trienes, pyrrole compounds could be isolated. The reactions of five-membered zirconacycloallenes with esters and isocyanates are shown in **Figure 36**. From carboxylic esters like ethyl acetate and methyl benzoate, after hydrolysis, alkynyl ketones were formed in low yields. Diethyl carbonate gave moderate yields of alkynyl esters. When the starting material has substituents at the 2,4-position (**67A**), by the insertion of phenylisocyanate into the Zr-C bond, an alkynyl amide could be obtained. In contrast, with silyl groups at the 2,5-position of the metallacycle (**67D**), after hydrolysis, dienyl amides were obtained.

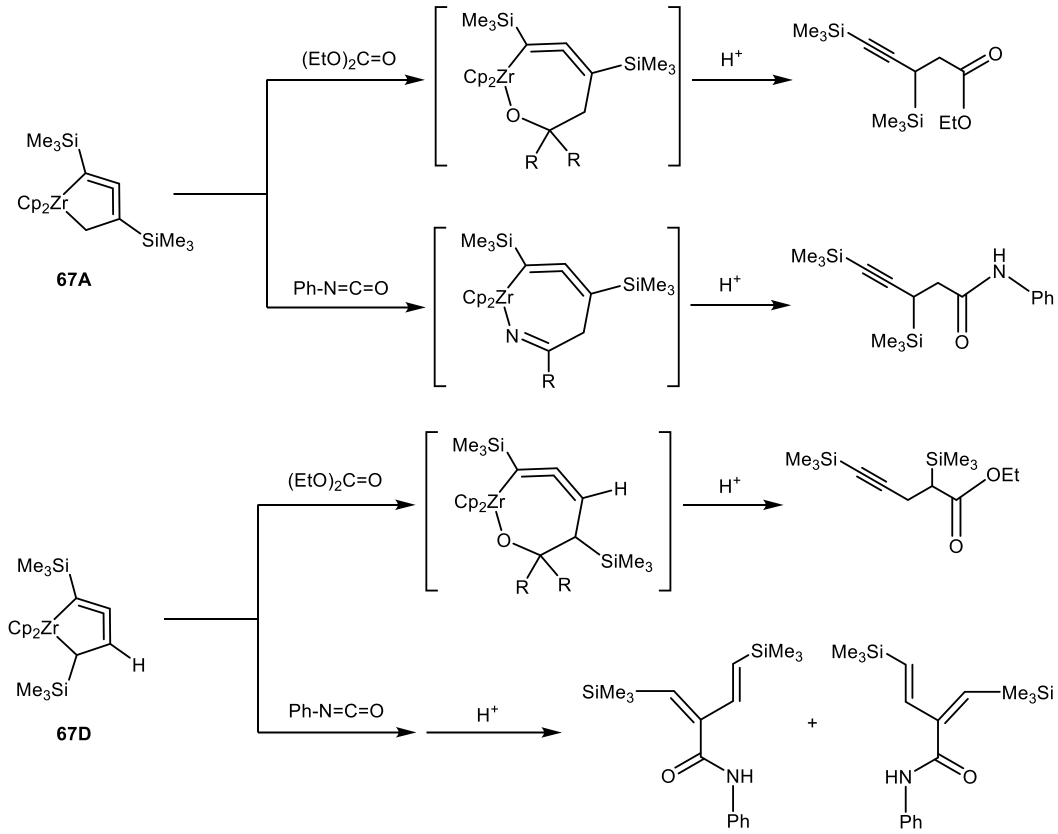


Figure 36. Reaction of 2,4- and 2,5-substituted 1-zirconacyclopent-2,3-dienes with esters and isocyanates.

Additionally, several C-C bond formation reactions of the described intermediated were realized. Via transmetallation to copper salts and subsequent addition of allyl halides, the allylated, highly funtionalized organic products were obtained (**Figure 37**). All these examples show the diverse reactivity of this class of unusual five-membered metallacycles that allows for the preparation of organic structures with a high degree of complexity that are either only accessible through multistep procedure, or not accessible at all.

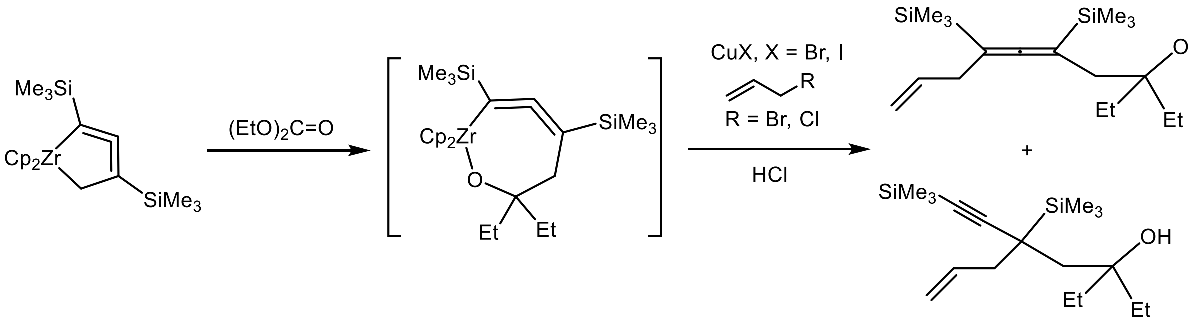


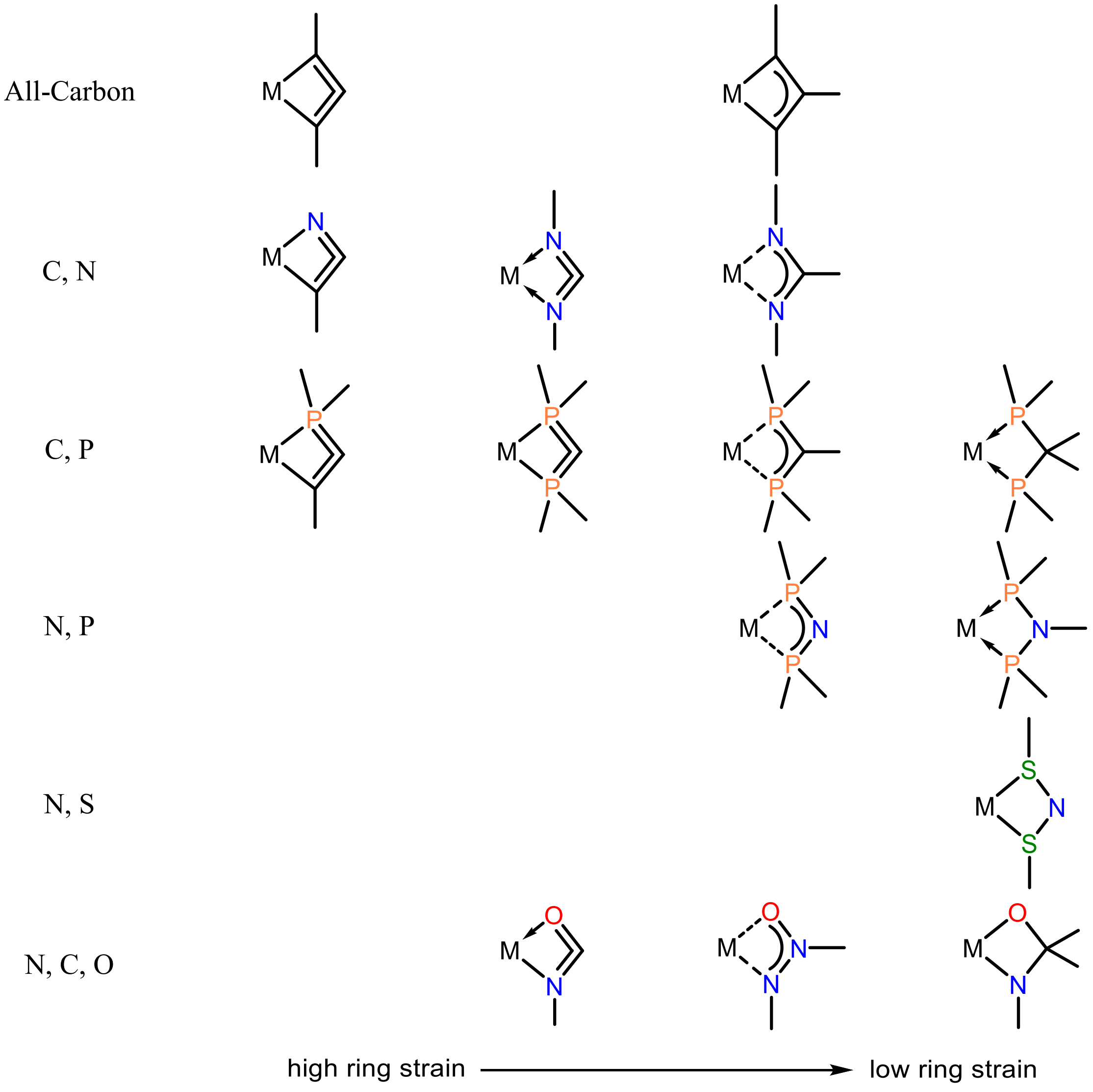
Figure 37. Insertion of ketones and reaction of the formed intermediates via transmetallation by copper salts with subsequent addition of allyl halides to yield allylated products.

A wide variety of interesting novel stoichiometric and catalytic C-C coupling and cleavage reactions of the five-membered group 4 complexes were found. Most of these highly functional reaction products have been found to be the result of unforeseeable reactivity rather than led by design. One of the reasons is the theoretical studies have shown that the description of these molecules is complicated because the influence of the metals, interacting with the unsaturated bonds in the ring.

1.3 Four-membered metallacycles

Following the development of the chemistry of three- and five-membered metallacycles, a series of metallacycles that seemed to "violated the norm" and thus be unstable were successfully synthesized and isolated. A lot of organometallics chemist made great efforts in this field and are continuing to challenge nature. A simple comparison of the structures of five-membered metallacycloallenes with two double bonds and metallacyclocumulenes with three double bonds in the five-membered ring system, led to the question, whether the smaller four-membered metallacycles, i.e., 1-metallacyclobuta-2,3-dienes, with two double bonds in the four-membered ring system could exist. The challenge of this question is whether high unsaturation and small ring systems can coexist, since it will then lead to the increasing ring strains, indicated by high strain energy, which will render the metallacycles highly unstable.

Table 1. Carbon-, nitrogen-, phosphorus-, sulfur- and oxygen-containing four-membered metallacycles.



According to the different types of atoms in the four-membered metallacycles, this class of compounds can be divided into two categories. One type is composed only of carbon and metal atoms, which is referred to as all-carbon four-membered metallacycles. The other type is a four-membered ring composed of heteroatoms such as N, P, O, S etc. and metal atoms (**Table 1**[68]). In this chapter the development history and current research progress of four-membered heterometallacycles will be briefly introduced (chapter **1.3.1**), followed by the discussion of all-carbon four-membered metallacycles (chapter **1.3.2**).

1.3.1 Four-membered heterometallacycles.

Emanating from the fact that highly strained metallacycles can be stabilized by incorporation of heteroatoms into the cyclic unit, group 15 elements with their additional lone pair are of tremendous interest. Especially suitable nitrogen containing ligands are in most cases easily accessible and offer a wide diversity of properties. The scope of nitrogen and carbon containing ligands is of overwhelming variety. Selected examples of nitrogen containing four-membered metallacycles are shown in **Figure 38**.

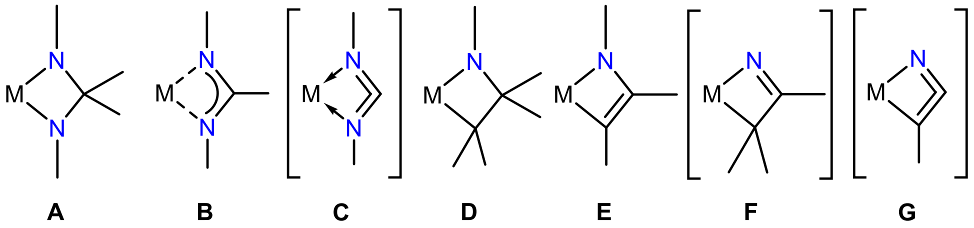


Figure 38. Selected examples of nitrogen containing four-membered metallacycles.

The saturated diazametallacyclobutanes (**A**) azametallacyclobutanes (**D**) do not exhibit ring strain in the metallacycle. Bergman and co-workers synthesized type **A** complexes with group 4 metals in 2000.[69] In these examples both cyclic C-N bond lengths are in the range of a typical single bond. The structural motif **D** was also reported by the Bergman group for a zirconocene complex, displaying only single bonds in the central metallacycle.[70] Another example was reported by the group of Beckhaus via formal [2+2] cycloaddition reaction of a carbodiimide to a titanallene intermediate [Cp*$_2$Ti=C=CH$_2$].[71]

Four-membered metallacycles of the type **B** are well known for group 4 metals although the incorporation of one double bond into the cyclic system leads to an increasing ring strain. Gambarotta and co-workers reported the zirconocene complex Cp$_2$Zr(Cl)[κ^2-N,N-[Cy-N-C(H)-N-Cy]] possessing amidinato ligands in **B** type.[72] The complex displaying the structural motif **F** without any substituent at the nitrogen atom and C=N double bond are hitherto unknown. However, complexes with only one nitrogen atom and a C=C double bond in the cyclic system (**E**) are easily accessible. [73] These compounds are either synthesized via [2+2] cycloaddition of an alkyne at a metal-imido species M=NR or by insertion reaction of a nitrogen containing substrate (azido- or diazo-compound) into the M-C bond of a metallacyclopropene. 1-Metallacyclodiazabuta-2,3-dienes (**C**) and metallacycloazabutadi-2,3-enes (**G**) were not isolated so far.

Another type of heterometallacycles containing phosphorus and nitrogen is well investigated. The κ^2-P,P coordination mode (**Figure 39**) is described for many transition metals such as Fe,[74] Ni,[75] Pd[76] and Pt.[74b]

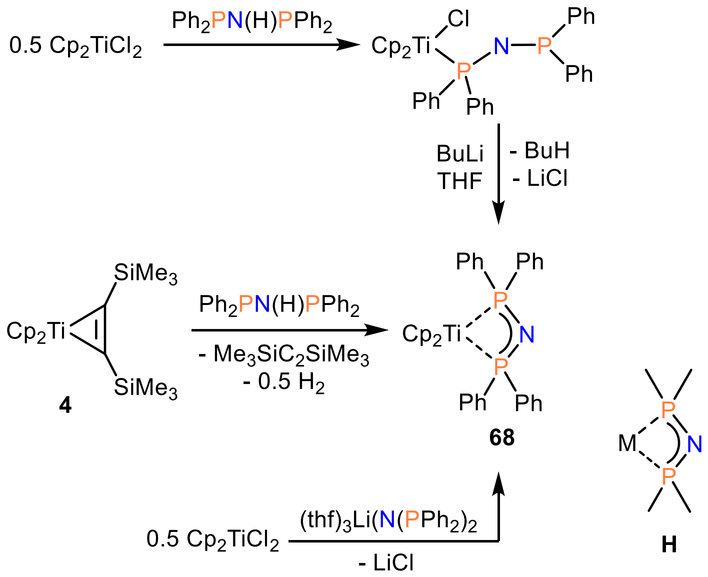


Figure 39. Synthesis of the titanocene complex [$Cp_2Ti\{\kappa^2$-*P,P*-$Ph_2PNPPh_2\}$] and κ^2-P,P coordination mode of a PNP ligand.

In 2012, Rosenthal and co-workers reported the synthesis of highly strained heterometallacycles of group 4 metallocenes with *N,N*-bis(diphenylphosphino)amide ligands. Complexes [$Cp_2Ti\{\kappa^2$-*P,P*-$Ph_2PNPPh_2\}$] (**68**, **Figure 39**) and [$Cp_2Zr\{\kappa^2$-*P,P*-$Ph_2PNPPh_2\}$] (**69**, **Figure 40**) were successfully synthesized and isolated using different methods.[77] In both cases, the metal center is in the oxidation state +3.

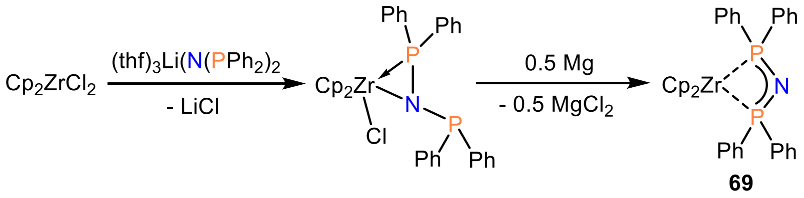


Figure 40. Synthesis of the zirconocene complex [$Cp_2Zr\{\kappa^2$-*P,P*-$Ph_2PNPPh_2\}$].

The chemistry of four-membered metallacycles with phosphorus and carbon containing ligand has been well documented over the last century. The majority of these complexes contains a neutral diphosphinomethane ligand R_2P-$C(R_2)$-PR_2 with a sp^3-hybridized carbon atom, which shows a small ring strain (**I**).

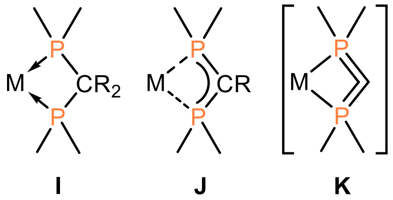


Figure 41. Different four-membered metallacycles with a PCP fragment.

The complexes with monoanionic diphosphinomethanide ligand $[R_2P\text{-}C(R)\text{-}PR_2]^-$ (**J**) with a sp^2-hybridized carbon atom have been well studied. Karsch and co-workers described a Zr[78] complex and an Fe [79] complex with such $[R_2P\text{-}C(R)\text{-}PR_2]$ ligand. The V complex $[Li(thf)_4][V\{\kappa^2\text{-}P,P\text{-}Ph_2PC(H)PPh_2\}_3]$ was synthesized by Gambarotta et al.[80] Karsch et al. prepared both the zirconocene complex $[Cp_2Zr(Cl)\{\kappa^2\text{-}P,P\text{-}Ph_2PC(SiMe_3)PPh_2\}]$[81] and the ate complex $[Li(tmeda)_2][Zr(Cl)_2\{\kappa^2\text{-}P,P\text{-}Ph_2PC(SiMe_3)PPh_2\}]$.[82] Additionally, they also reported the titanocene complex $[Cp_2Ti\{\kappa^2\text{-}P,P\text{-}Ph_2PC(SiMe_3)PPh_2\}]$ in 1993.[83] The dianionic diphosphinomethandiide ligand (**K**) with a *sp*-hybridized carbon atom would contain two P(V) atoms in the cyclic unit and the desired allene moiety to result in a highly strained cyclic system.

In 2013, Rosenthal and co-workers reported the synthesis of group 4 metallacycles with bis(diphenylphosphino)methanide ligands. The lithium bis(diphenylphosphino)methanides were prepared in-situ by the deprotonation reaction of diphosphinomethanes $Ph_2PC(H)(R)PPh_2$ (R = H, $SiMe_3$) with *n*-BuLi. Subsequent salt metathesis reaction with Cp_2TiCl_2 yielded the titanocene complexes **70-H** and **70-SiMe₃**. The complex **70-SiMe₃** can also be obtained from the reaction of $Ph_2PC(H)(SiMe_3)PPh_2$ with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ at 60 °C (**Figure 42**).[84]

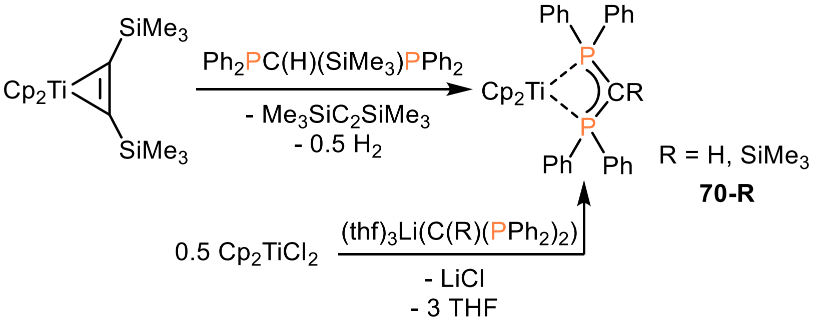


Figure 42. Synthesis of the titanocene complexes **70**.

The related zirconocene hydrido complex **71** and hafnocene chloride complexes **72-H**, **72-SiMe₃** were prepared from lithiated bis(diphenylphosphino)methane, reacted with Schwartz reagent $[Cp_2ZrClH]$ and $[Cp_2HfCl_2]$, respectively (**Figure 43**).

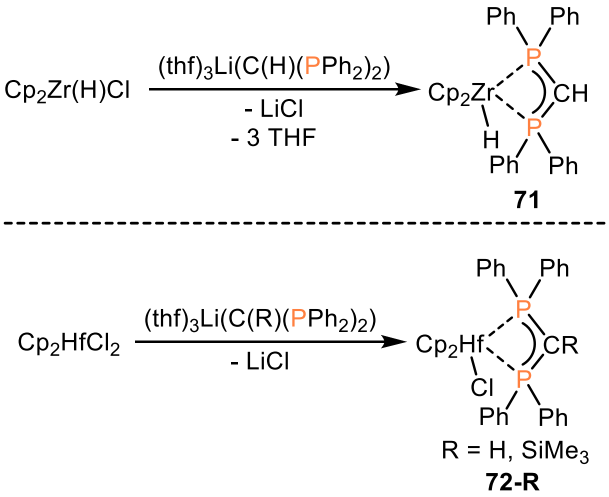
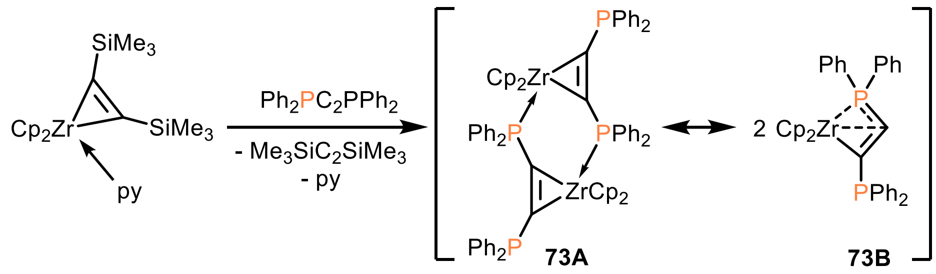


Figure 43. Synthesis of the zirconocene hydrido complex **71** and hafnocene chlorido complexes **72-R**.

In the same year, Rosenthal and co-workers obtained the structural motif **K** (**Figure 41**) by reacting two molecules of **8-py** with one equivalent of diphosphinoalkyne, resulting in the formation of complexes **73A** and **73B** as a mixture (**Figure 44**, top). In the ^{31}P NMR spectrum, two different resonances appear at 15.3 and 8.4 ppm, clearly indicating the dimeric nature of complex **73A** in solution. Besides these two signals, a different set of resonances appears at 12.0 and -15.7 ppm with a P-P coupling constant $^3J = 190.2$ Hz, which was tentatively assigned to the structure of the four-membered metallacycle **73B**, the possible resonance form of the monomeric **73B** (**Figure 44**, bottom).[85]

synthesis of complex ***73***



resonance forms of monomeric complex ***73B*** *in solution*

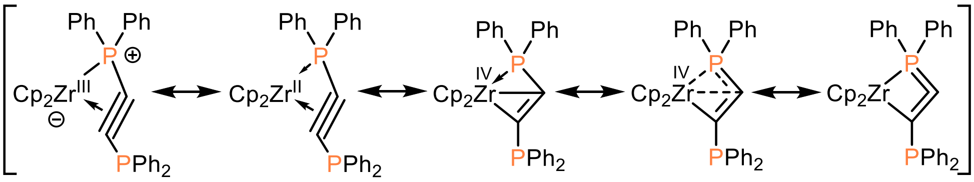
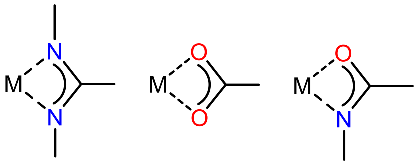


Figure 44. Synthesis of the complex **73A** and resonance with monomeric **73B**, top; possible resonance forms of the monomeric complex **73** in solution.

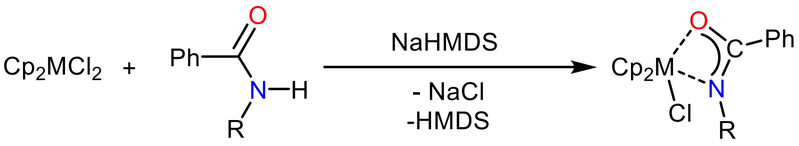
Group 4 metallocene complexes with amidinato ligands (**B**) are well described (**Figure 45**). Based on the isolable relationship O→NR, the exchange of both NR fragments by oxygen atoms leads to carboxylate complexes (**L**), a class of ligands, which is also known for numerous group 4 metallocene complexes. The replacement of only one NR fragment by an oxygen atom, leading to amidato ligands (**M**) is another important class of ligands.



B **L** **M**

Figure 45. Different isolobal ligands: amidinato (**B**), carboxylate (**L**) and amidato (**M**).

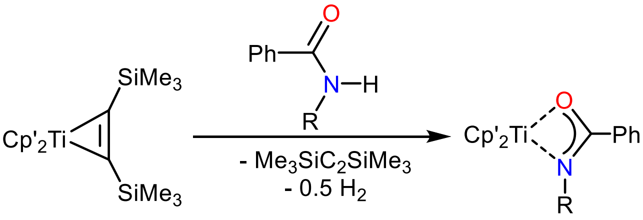
The four-membered heterometallacyclic complexes of group 4 metallocenes with amidato ligands (**B**) were reported by Rosenthal and co-workers in 2014.[86] Deprotonation of suitable precursors such as N-(2,6-diisopropylphenyl)benzamide or benzanilide with NaHMDS in toluene, followed by a salt metathesis reaction with Cp_2ZrCl_2 resulted in the formation of the four-membered heterozirconacycles **74** according to **Figure 46**. In a similar procedure, the Hf complex **75** was formed by using benzanilide.



74 M = Zr, R = Ph, Dipp
75 M = Hf, R = Ph

Figure 46. Synthesis of the chloride complexes **74** and **75**.

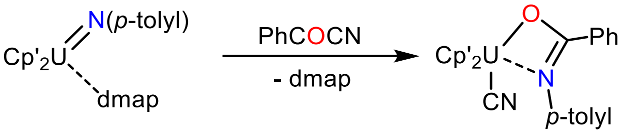
The reaction of benzanilide with the titanocene sources **4** and **5** in toluene at elevated temperature resulted in the formation of paramagnetic Ti^{III} complexes $[Cp'_2Ti\{\kappa^2\text{-}O,N\text{-}PhNC(Ph)O\}]$ (Cp’ = Cp, Cp*) (**76** and **77**) in good yields (**Figure 47**).



76 Cp' = Cp, R = Ph, Dipp
77 Cp' = Cp*, R = Ph

Figure 47. Synthesis of the titanocene complexes **76** and **77**.

Following another approach for construction of the heterometallacycle, Walter and co-workers reported the reaction of the Uranium imido metallocene $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2U{=}N(p\text{-tolyl})(dmap)$ with one equivalent of PhCOCN at 50 °C, leading to release of the dmap ligands and formation of the [2+2] cycloaddition product $[\eta^5\text{-}1,3\text{-}(Me_3C)_2C_5H_3]_2U[OC(Ph)N(p\text{-tolyl})](CN)$ (**78**, **Figure 48**).[87]



Cp' = 1,3-$(Me_3C)_2C_5H_3$ **78**

Figure 48. [2+2] cycloaddition of Uranium imido complex.

1.3.2 *All*-carbon four-membered metallacycles.

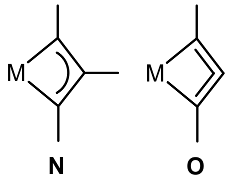


Figure 49. All-carbon four-membered metallacycles.

According to the substitution pattern, the class of *all*-carbon metallacyclobutadienes can be divided into β-C substituted (**N**) and β-C non-substituted (**O**) derivatives (**Figure 49**). The first β-C substituted metallacyclobutadiene, the iridacycloutadiene $[IrCl(CO)(PMe_3)_2(C_3Ph_3)]BF_4$ **79** (**Figure 50**), was reported in 1970.[88]

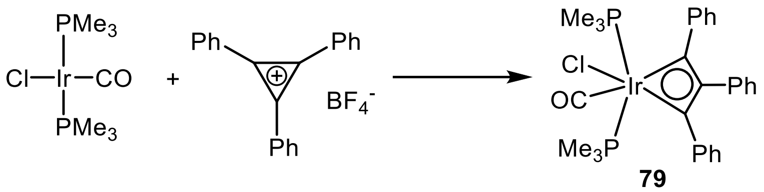


Figure 50. Synthesis of iridacyclobutadiene **79**.

Since then, a number of other metallacyclobutadienes have been isolated and thoroughly characterized, especially for those that contain transition metals of group 5-9. These compounds were mostly discussed in the context of alkyne metathesis reactions.[89] Furthermore, these complexes were also used as starting materials for the synthesis of organometallic compounds such as metallabenzene, η^5-cyclopentadienyl, and η^3-cyclopropenyl complexes. In addition, as these species are metal analogues of cyclobutadienes, these complexes are also of fundamental importance in view of the intense interest in ring-strained and conjugated metallacycles. In the following sections, several strategies for the synthesis of such unusual organometallics are summarized.

a) Deprotonation of β-CH proton to synthesize all-carbon metallacyclobutadienes. The reactions of terminal alkynes with high-valent carbyne complexes of tungsten and molybdenum are rather complex. Metallacyclobutadienes were obtained occasionally from these reactions. For example, Schrock and co-workers showed that treatment of the carbyne complexes [W(≡CCMe$_3$)(dipp)$_3$] (**80)** and [W(≡CCMe$_3$)(dmp)$_3$(thf)] (**81**, dmp = OC$_6$H$_3$-2,6-Me$_2$) with Me$_3$CC≡CH produced the tungstacyclobutadienes (**80**), respectively. Similar tungstacyclobutadienes **83-85** were produced from the reactions of terminal alkynes with the carbyne complexes [W(≡CCMe$_3$)Cl(dipp)$_3$], [W(≡CCMe$_3$){OCH(CH$_3$)$_2$}$_3$], and [W(≡CPh){OCH(CH$_3$)$_2$}$_3$], respectively (**Figure 51**).[90]

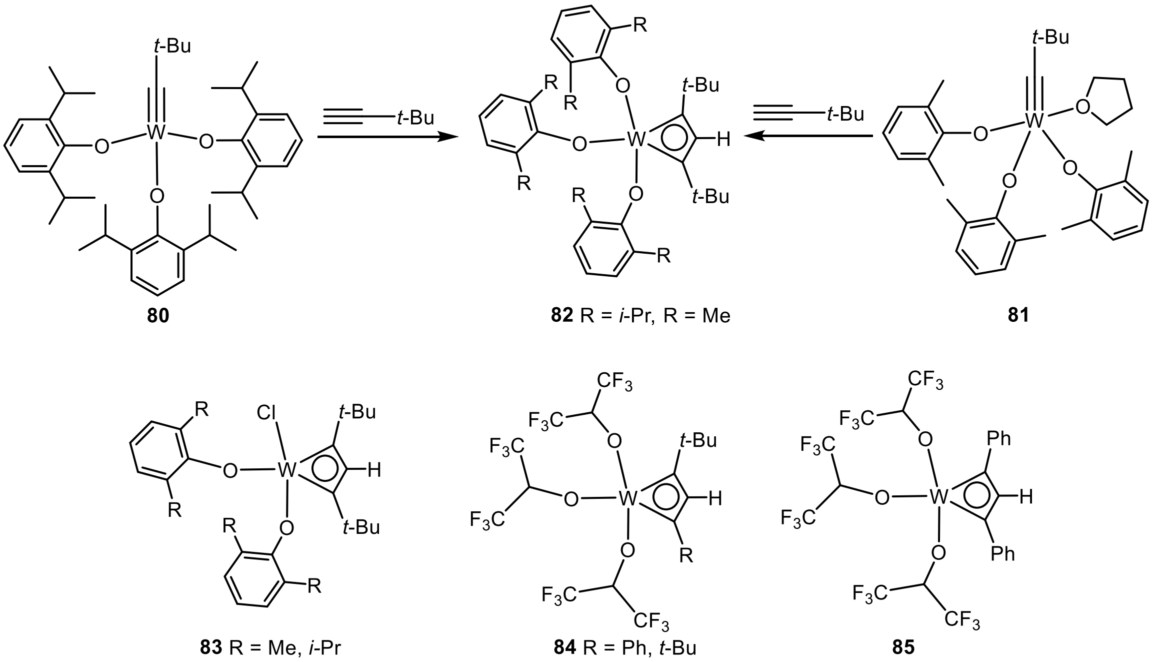


Figure 51. Tungstacyclobutadienes from reactions for terminal alkynes with carbyne complexes.

The β-CH protons of above-mentioned complexes are acidic and can be easily removed by deprotonation. For example, the tungstacyclobutadienes **83** were treated with NEt_3 to produce the deprotio-tungstacyclobutadienes **86** (**Figure 52**).[90a]

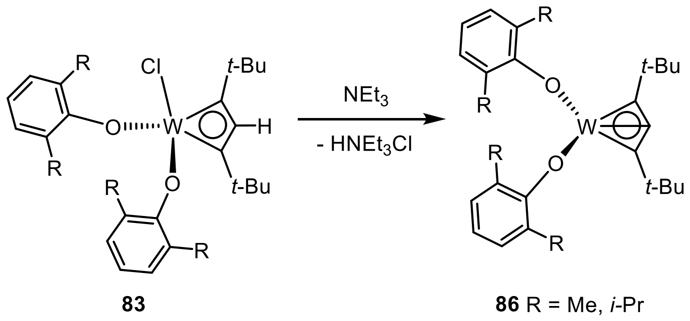


Figure 52. Deprotonation reactions of metallacyclobutadienes.

Similarly, the tungstacyclobutadiene [W{C(CMe_3)CHCR}{OCH(CF_3)$_2$}$_3$] (**84**, R = Ph, *t*-Bu) was treated with pyridine to give the *deprotio*-tungstacyclobutadiene complexes (**87**, R = Ph, *t*-Bu). Complex **84** also reacted with DME in the presence of NEt_3 to give the unsymmetrically substituted deprotio-tungstacyclobutadiene **88** (**Figure 53**).[90a]

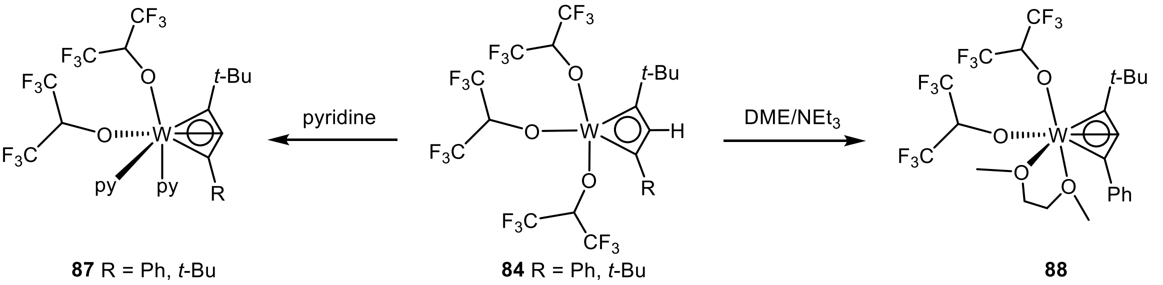
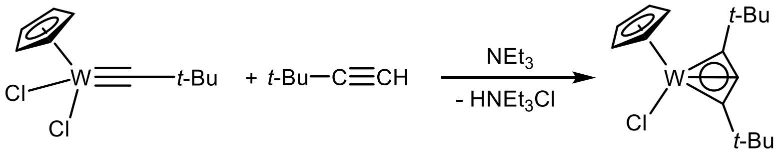


Figure 53. Deprotonation reactions of metallacyclobutadienes.

Other metallacyclobutadienes that can be deprotonated by pyridine to give deprotio-metallacyclobutadienes include complexes [W{C(CMe_3)CHC(CMe_3)}(dipp)$_3$] and [W{C(CMe_3)CHC(CMe_3)}(dmp)$_3$].[90a] These complexes were found to slowly convert into [W(C_3(CMe_3)$_2$)(OAr)$_2$] and free phenols in benzene at 25 °C. It has also been reported that the tungstacyclobutadiene [W{C_3(CMe_3)D}{OCH(CF_3)$_2$}$_3$] undergoes a D/H exchange reaction with $(CF_3)_2CHOH$ at room temperature in C_6D_6 to give [W{C_3(CMe_3)H}{OCH(CF_3)$_2$}$_3$], presumably through reversible protonation and deprotonation.

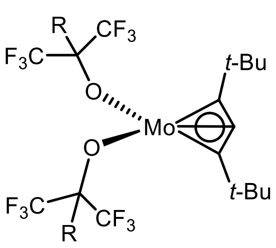
b) Reaction of carbyne complexes with terminal alkynes to synthesize all-carbon metallacyclobutadienes. The carbyne complex [CpW(≡CCMe$_3$)Cl$_2$] can react with Me$_3$CC≡CH in the presence of NEt$_3$ to also give the deprotio-tungstacyclobutadiene [CpW(C$_3$(CMe$_3$)$_2$)Cl] **89** (**Figure 54**).[91] In this study the authors found that complex [CpW(≡CCMe$_3$)Cl$_2$] will not metathesize alkynes. On the other side, when reacting with Me$_3$CC≡CH, [CpW(≡CCMe$_3$)Cl$_2$] gave the complex **89** and a [CpCl$_3$W=C-(CMe$_3$)[*trans*-HC=CH(CMe$_3$)]] complex.



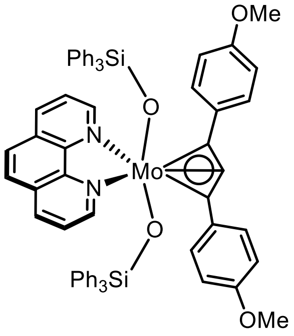
89

Figure 54. Example of a reaction of a carbyne complex with terminal alkynes and base to give a deprotio-metallacyclobutadiene.

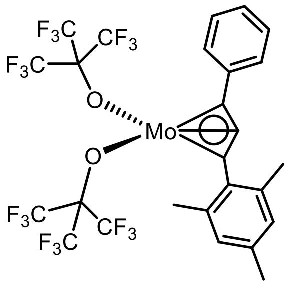
Besides W(VI), there are many reported reactions of Mo(VI) carbyne complexes with terminal alkynes to give deprotio-metallacyclobutadienes. For example, the carbyne complexes [Mo(≡CCMe$_3$){OCR(CF$_3$)$_2$}$_3$(dme)] (R = Me , R = CF$_3$) reacted with one equivalent of Me$_3$CC≡CH to give the deprotio-molybdenacyclobutadiene [Mo{C$_3$(CMe$_3$)$_2$}{OCR(CF$_3$)$_2$}$_3$] (**90**, R = M, CF$_3$) (**Figure 55**).[92] In 2012, Fürstner and co-workers reported the formation of the Mo complex **91** that could be obtained when treating the carbyne complex [Mo(≡PhOMe){(OSiPh$_3$)$_3$}] with the 4-methoxyphenylacetylene followed by the coordination of the N-donor ligand 1,10-phenanthroline.[93] In 2019, Tamm and co-workers[94] also found the formation of [Mo{(OC(CF$_3$)$_3$)$_2$}(PhC$_3$Mes)] (**92**) in the reaction of [Mo(≡CMes){(OC(CF$_3$)$_3$)$_3$}] with phenyacetylene, which is similar to Schrock's studies in 1985.



90 R = Me, CF$_3$
Schrock



91
Fürstner

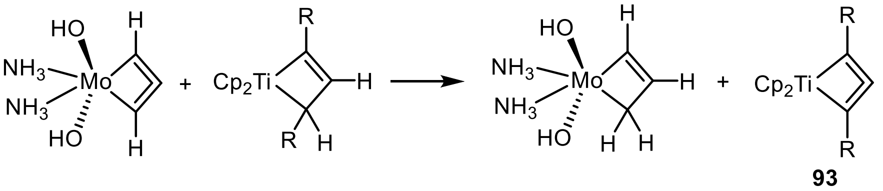


92
Tamm

Figure 55. Examples of reactions of Mo carbyne complexes with terminal alkynes to give a deprotio-metallacyclobutadienes.

c) Salt metathesis reaction between a 1,3-dilithiated allene precursor and group 4 metallocene dihalide complex. The reactions discussed in sections a) and b) most likely proceed through deprotonation of a metallacyclobutadiene intermediate. Formation of deprotio-metallacyclobutadienes has also been reported for reactions of terminal alkynes with carbyne complexes [Mo(≡CCMe$_3$)(O$_2$CCF$_3$)$_3$(dme)],[95] [W(≡CPh){OCH(CF$_3$)$_2$}$_3$(dme)][90a] and [W(≡CCMe$_3$){OCMe$_3$}$_3$].[96]

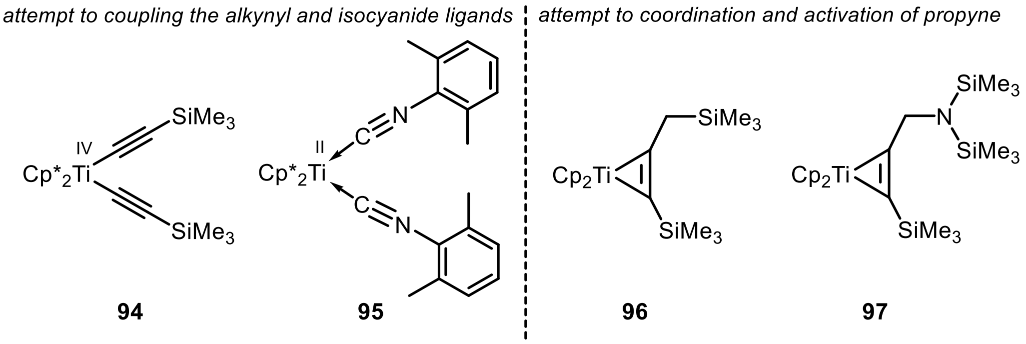
Up to the starting point of this PhD project in 2020, the chemistry of highly strained four-membered all-carbon metallacycles of group 4 metals was very limited. Jemmis, Schulz, Rosenthal and co-workers reported theoretical evidence of stabilization of four-membered 1-metallacyclobuta-2,3-dienes (termed as "metallacycoallenes") by using group 4 metal fragments. They have shown from a comprehensive theoretical study that a group 4 metal can stabilize the exotic four-membered metallacycloallene (**93**) by interacting with the central carbon atom of the MC_3 ring along with two strong terminal M-C bonds. Substituents, such as acyclic and cyclic alkylated amines like NMe_2 and piperidino, as well as NHCs, which are capable of donating two electrons to the ring system of the complex, were suggested stabilize it significantly to make it synthetically viable (**Figure 56**).



R	H	Ph	CH_3	NH_2	NMe_2	Piperidino	NHC	CO
Δ G	17.2	9.7	13.8	-0.6	-8,4	-8,6	-3.7	-6.6

Figure 56. Isodesmic equation for complex **93** (R = H, Ph, CH_3, NH_2, NMe_2, piperidino, NHC, CO) and ΔG [kcal mol^{-1}] calculated at the BP86/def2-SVP level of theory.

Following up to this, our group have attempted to access this class of compounds using different approaches. First, coordination and coupling reactions at group 4 metallocene complexes with carbodiimides, nitriles, and isonitriles as reaction partners were studied. Alkynyl and isocyanide ligands were installed at Ti to study the potential thermos- or photochemical coupling of these groups to furnish a four-membered aza-titanacycle. Related transformations were discussed before by Mach and co-workers.[97] However this approach only resulted in the redox disproportionation of the Ti(III) complex, giving a Ti(IV) bis(alkynyl) complex (**94**) and a Ti(II) bis(isocyanide) species (**95**) (**Figure 57**).[98] Another attempt is by coordination of propyne derivatives bearing methylene groups adjacent to the coordinated alkyne triple bond, followed by in situ twofold deprotonation, which is introduced by our group in 2017. However, only coordination products **96** and **97** formed.[99] Unfortunately, all of these attempts did not lead to the formation of a group 4 1-metallacyclobuta-2,3-diene.


attempt to coupling the alkynyl and isocyanide ligands | *attempt to coordination and activation of propyne*

94 **95** **96** **97**

Figure 57. Complexes isolated during attempts to synthesize group 4 1-metallacyclobuta-2,3-dienes.

In 2018, our group reported the synthesis of a dizirconacyclooctatetraene using 1,3-dilithio-1,3-bis(trimethylsilyl)allene (**98**) as precursor (**Figure 58**).[100] The original purpose of this work was to synthesize 1-zirconacyclobuta-2,3-diene complex, although it was not successfully isolated, but for the very first time the aimed molecule was detected under MS conditions. The successful synthesis and isolation of 1,3-dilithio-1,3-bis(trimethylsilyl)allene as precursor can be regarded as a crucial step and a breakthrough for further studies. This dilithiated compound was first reported in the early 1990s by Barton and co-workers,[101] its large-scale synthesis, purification and isolation was however not reported before.

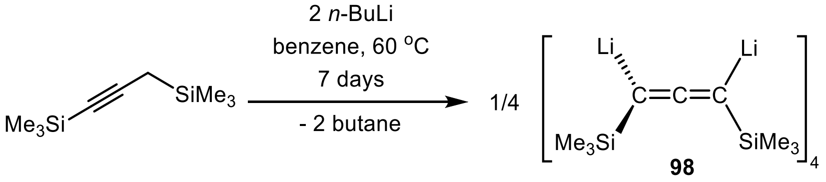


Figure 58. Optimized synthesis of 1,3-dilithio-1,3-bis(trimethylsilyl)allene (**98**).

Eventually, the first all-carbon group 4 1-metallacyclobuta-2,3-diene complex could be synthesized and isolated in 2019 by our group.[102] The synthesis of [*rac*-(ebthi)Ti{κ^2-*C,C*-($Me_3SiC_3SiMe_3$)}] (**99**) was achieved by reacting the *ansa*-metallocene dichloride [*rac*-(ebthi)$TiCl_2$] with 1,3-dilithio-1,3-bis(trimethylsilyl)allene (**98**, **Figure 59**). For the first time, it was shown that through combination of suitable metal center, cyclopentadienyl ligand and substituents at the C_3 unit the synthesis of all-carbon 1-metallacyclobuta-2,3-diene based on a group 4 metal is possible. This compound represents a formal metallacyclic analogue of non-existent 1,2-cyclobutadiene. Analysis of the structure and bonding reveals contributions of a highly unusual interaction of a formal Ti(III) fragment and an organic monoanionic radical with antiferromagnetic coupling between both radical centers, resulting in an open shell singlet species.

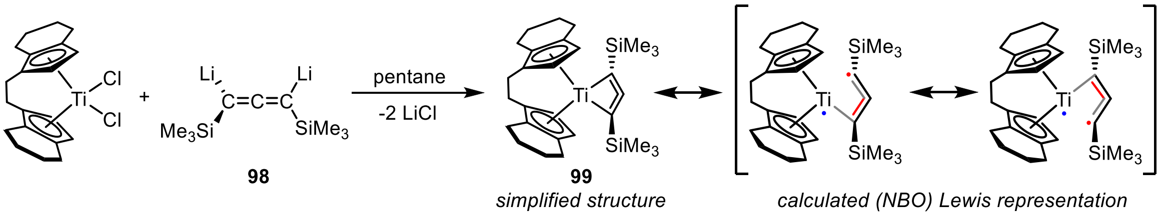


Figure 59. Synthesis of complex **99**.

As part of the present PhD project, we have later extended this class of complexes from titanium to zirconium (publication 1, section **4.1**).[103] Based on similar reaction routes, the complexes [Cp'$_2$Zr{κ^2-*C,C*-($Me_3SiC_3SiMe_3$)}] (**100**, Cp' = *rac*-ebthi; **101**: Cp' = Me_2Si-thi (thi = η^5-tetrahydroindenyl)) were successfully synthesized (**Figure 60**). As a difference to the related Ti complex, both compounds **100** and **101** undergo selective thermal C-H activation at the 7-positon of the tetrahydroindenyl fragment of the metallocene scaffold to produce a new type of "tucked-in" metallocene complex **100A** and **101A**.

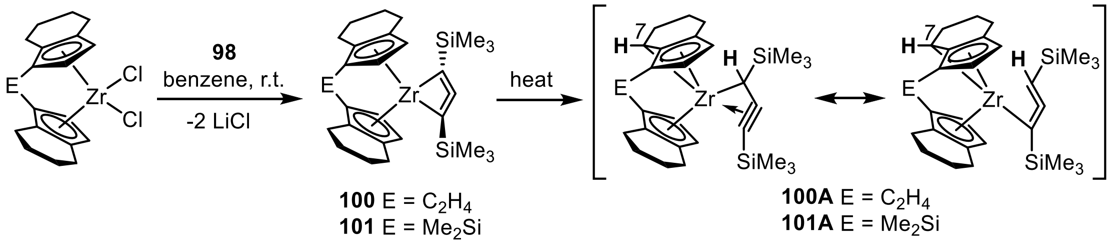


Figure 60. Synthesis of complexes **100** and **101** and their intramolecular C-H activation, leading to the formation of complexes **100A** and **101A**.

In order to avoid this intramolecular aliphatic C-H bond activation, we have later used *ansa*-η^5-indenyl instead of *ansa*-η^5-tetrahydroindenyl ligands (**Figure 61**, publication 2, section **4.2**). This simple modification prevents previously reported C-H activation at the backbone of the cyclopentadienyl ligand and thus makes these complexes promising candidates for the study of the reactivity of this class of compounds.[104]

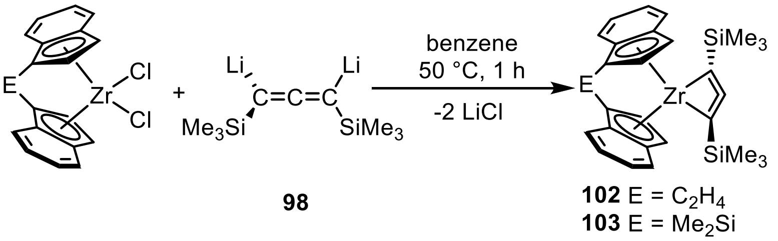


Figure 61. Synthesis of complexes **102** and **103**.

By using the same 1,3-dilithio-1,3-bis(trimethylsilyl)allene (**98**) as precursor, Mindiola and co-workers prepared two 1-metallacyclobuta-2,3-diene complexes [(BDI)M{κ^2-*C,C*-($Me_3SiC_3SiMe_3$)}] (M = Ti, V; BDI = $[ArNC(CH_3)_2]_2CH^-$, Ar = 2,6-$^iPr_2C_6H_3$, **Figure 62**) with a bidentate non-Cp ligand. Both complexes are paramagnetic.[105]

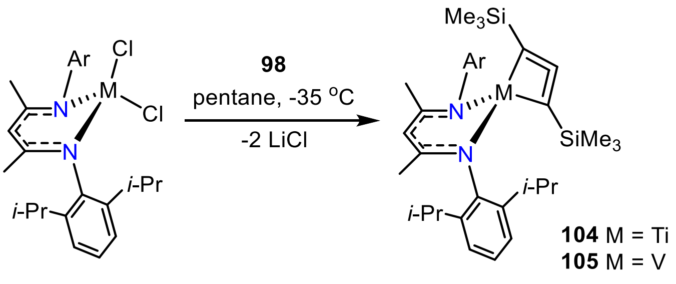


Figure 62. Synthesis of complex **104** and **105**.

Table 2 shows that the geometrical configuration of the four-membered metallacycles can be correlated to the number of d-electrons. For the complex **99** with Ti as metal center, the metallacycle possesses longer M-C$_\alpha$ and longer M-C$_\beta$ bonds and larger C-C-C angles compared to Zr, V, Mo and W as metal center. On the other hand, with a group 6 metal as the central atom, the bond length of M-C$_\alpha$ and M-C$_\beta$ decrease, as well as the C-C-C angle.

Table 2. Selected average bond lengths and angles for complexes **87-*t*-Bu**, **89**, **91**, **99**, **104** and **105**.

Complexes	M-C$_\alpha$ Avg. bond length (Å)	M-C$_\beta$ Avg. bond length (Å)	C$_\alpha$-C$_\beta$ Avg. bond length (Å)	C$_\alpha$-C$_\beta$-C$_\alpha$ Angle (°)
87-*t*-Bu	1.974	1.943	1.379	134.3
89	1.924	2.049	1.355	130.2
91	1.996	1.979	1.373	135.2
99	2.203	2.235	1.306	150.1
104	2.068	2.073	1.324	142.3
105	1.890	1.971	1.380	131.9

The reactivity of theses all-carbon four-membered metallacycles also have been studied once they are prepared. Exposition of [*rac*-(ebthi)Ti{κ^2-*C,C*-($Me_3SiC_3SiMe_3$)}] solution to air and moisture lead the formation of propyne $Me_3SiC{\equiv}CH_2SiMe_3$ and eventual decomposition. In reactions with TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) formation of undefined reaction mixture containing Ti(III) species occurs. When reacting with carbonyl compounds, the 1,3-enynes (**108**) formed. A computational study shows that **106** and **107** are possible intermediates, which indicate that the insertion of the C=O bond into the M-C bond is the first step of the reaction (**Figure 63**).[102]

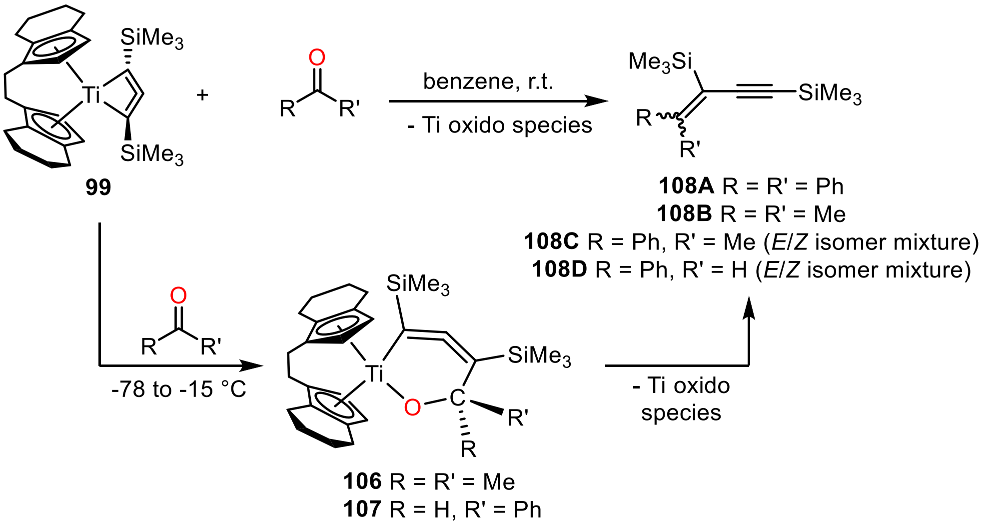


Figure 63. Reaction of complex **99** with carbonyl compounds.

Reaction of the corresponding Zr complexes **100** and **101** with carbonyl compounds shows the same behavior as complex **99** (**Figure 64**). However, in these cases six-membered oxa-zirconacycles **109** and **110** can be isolated and characterized as intermediates, which is nicely consistent with DFT results, leading to the formation of 1,3-enyne products (**115**).[103]

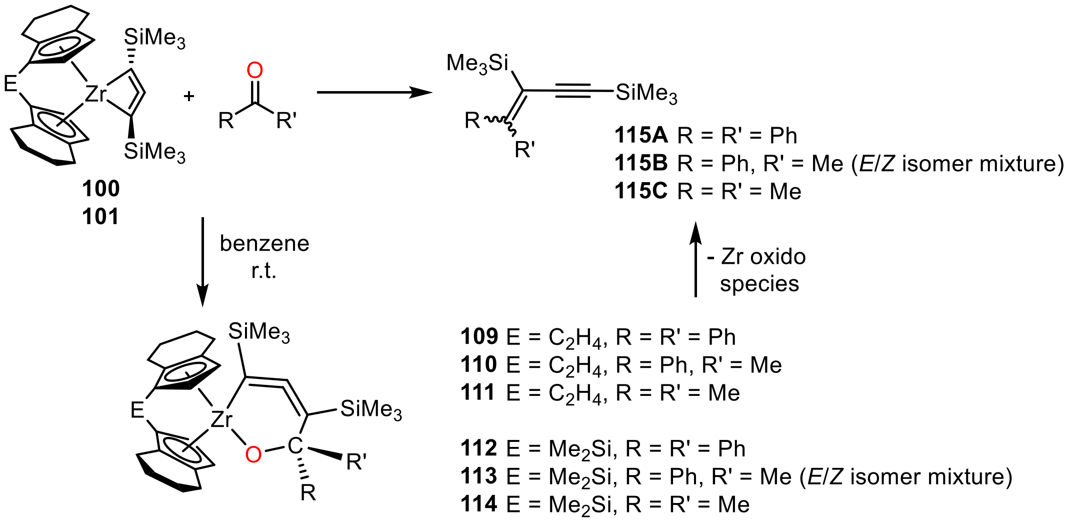


Figure 64. Reaction of complex **100** and **101** with carbonyl compounds.

The reaction of complexes **99**, **100** and **101** with differently substituted carbodiimides RN=C=NR (R = Cy, *i*-Pr, *p*-Tol, $SiMe_3$) resulted in two different types of products. The four-membered 2-aza-1-metallacyclobut-3-enes formed when R = Cy, *i*-Pr, *p*-Tol (**119**). On the other hand, the six-membered 2-aza-1-metallacyclohexa-2,4,5-trienes (**117**, **118**) formed when R = $SiMe_3$ (**Figure 65**). The different reactivity can be explained by the nature of $SiMe_3$ migration event. Details of this can be found in publication 2 (section **4.2**).[104]

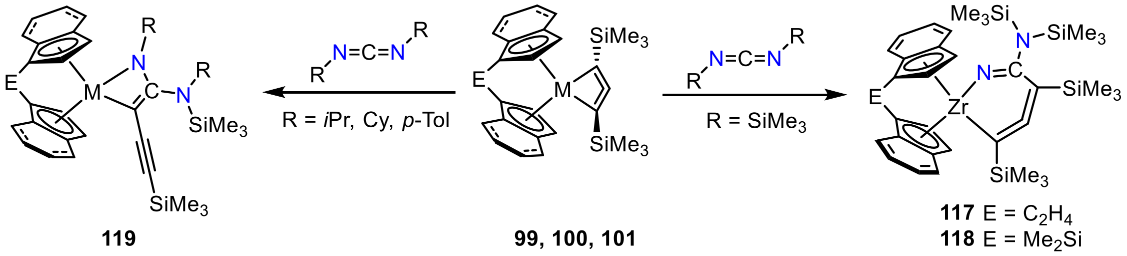


Figure 65. Reaction of complex **99**, **100** and **101** with carbodiimides.

Complexes with this 1-metallacyclobuta-2,3-diene motif were discussed in the past as catalytically relevant intermediates or precursors to catalytically active carbyne complexes in alkyne polymerization. In fact, Mindiola and co-workers could show that both complexes **104** and **105** exhibit catalytic activity in the polymerization of phenylacetylene to form cyclic-polyphenylacetylene.

In previous results, we have shown that the $SiMe_3$ group is able to stabilize the dilithioallene precursor as well as the respective 1-metallacyclobuta-2,3-dienes. However, this was for a long time limited to $SiMe_3$. In this regard, a part of this work is to explore other potential substituents that can also give access to suitable ligand synthons and 1-metallacyclobuta-2,3-dienes. Here, we introduce two new phenyl-substituted dilithiated ligand precursors that can be used for the preparation of four new 1-

metallacyclobuta-2,3-dienes bearing [*rac*-(ebthi)M] as the metallocene unit. Furthermore, the consequences of electronic and steric modification of 1-metallacyclobuta-2,3-dienes are also studied spectroscopically and electrochemically in this part. Details can be found in publication 3 (section **4.3**).

The coordination and activation of azo-compounds at early transition metal fragments has great potential, resulting in imido- or hydrazido complexes that are discussed to play a play a key role in nitrogen activation and fixation, heterocycle synthesis and atom and group transfer processes. The 1-metallacyclobuta-2,3-dienes with highly strained rings are good templates to synthesize these complexes. Hence, another part of this PhD thesis focuses on the investigation of the reactivity of 1-metallacyclobuta-2,3-diene with diazenes, aiming at the characterization of the reaction products and an in depth understanding of the reaction mechanisms, giving further insights into redox properties of these unusual complexes. Details of this part can be found in publication 4 (section **4.4**).

2 Objectives

Cyclobutadienes are excellent examples of antiaromatic compounds that have been studied extensively both experimentally and theoretically. Due to a combination of their antiaromatic ground state and high ring strain, cyclobutadiene derivatives are in general highly reactive species that cannot be easily isolated unless they are kinetically stabilized with suitable protecting groups. 1-metallacyclobuta-2,3-dienes are a group of organometallic compounds that can be regarded as complexes derived from the formal replacement of a CR_2 group in a cyclobutadiene with an isolobal metal fragment. Different from cyclobutadienes, metallacyclobutadienes can be significantly more stable. Such four-membered metallacycloallene complexes were published before only for group 6 metals. Synthesis of such compounds is possible by coupling of a metal carbyne complex [M≡CR] with a terminal alkyne and subsequent deprotonation. Alternatively, these complexes are formed in alkyne metathesis as decomposition products of the alkylidyne catalyst and a reaction with a terminal alkyne. With the successful isolation of 1,3-dilithio-1,3-bis(trimethylsilyl)allene, the first group 4 1-metallacyclobuta-2,3-dienes with an *ansa*-metallocene ligand could be synthesized.

As an objective of this work, extension of the scope to other metallocene scaffolds was investigated, allowing for an investigation of structure- reactivity relationships. Furthermore, a variation of the metallacycle scaffold from bis-trimethylsilyl substitution to other substituents could allow for a generalization of the synthesis concept and a further broadening of the scope of available metallacycles. This would be key for a more general study of the reactivity of these complexes for stoichiometric and catalytic transformations such as alkyne polymerization. Thus, a second objective of this work was to explore the possibility of the existence of other group 4 1-metallacyclobuta-2,3-dienes with different substituents by synthesis of different 1,3-dilithiated precursors and try to explain the stabilizing relationship between substituents and 1-metallacyclobuta-2,3-dienes.

In general, the chemistry of highly strained metallacycles is of particular interest to realize unusual bonding situations that can pave the way to new types of ligand architectures or new chemical transformations. The group 4 1-metallacyclobuta-2,3-dienes are a well-suited platform for the realization of unusual geometries and bond situations by formation of metallaheterocycles through stoichiometric reaction with small molecules like ketones, nitriles, isocyanides, carbodiimides and diazenes. These metallaheterocycles can be regarded intermediates for a variety of catalytic organic transformations, which provide a good opportunity for the chemists to investigate the mechanisms of bond formation and cleavage. So, the third objective of this work was to investigate the reactivity of -metallacyclobuta-2,3-diene complexes towards small molecules and understand the bonding situations of the resulting products, as well as its formation mechanisms.

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4 List of publications

This chapter contains the original papers in which the presented results were published. The own contribution of author of the dissertation to each publication is highlighted separately.

Publication 1: Xinzhe Shi, **Sihan Li**, Melanie Reiß, Anke Spannenberg, Thorsten Holtricter-Rößmann, Fabian Reiß and Torsten Beweries, *Chem. Sci.* **2021**, *12*, 16074-16084.

"*1-Zirconacyclobuta-2,3-dienes: synthesis of organometallic analogs of elusive 1,2-cyclobutadiene, unprecedented intramolecular C-H activation, and reactivity studies*"

The work I undertook is the synthesis of the dilithiated allene precursor and the complex 19 as well as a minor part of the characterization was done by me. In addition, a minor part of the supporting information corresponding to the paper was written by me. Contribution to this paper is 20%.

Publication 2: Xinzhe Shi, **Sihan Li**, Anke Spannenberg, Fabian Reiß and Torsten Beweries, *Inorg. Chem. Front.* **2023**, *10*, 3584-3594. (**2023** HOT articles)

"*Selective 1,2-insertion of carbodiimides and substrate-divergent silyl group migration at 1-metallacyclobuta-2,3-dienes*"

The work I carried out is a half experiments and analyzed the characterization data. In addition, one-third of supporting information and the reactivity with carbonyl compounds in the paper was wiitten by me. Contribution to this paper is 40%.

Publication 3: **Sihan Li**, Mirjam Schröder, Adrian Prudlik, Xinzhe Shi, Anke Spannenberg, Jabor Rabeah, Robert Francke, Björn Corzilius, Fabian Reiß and Torsten Beweries, *Chem. Eur. J.* **2024**, e202400708.

"*A General Concept for the Electronic and Steric Modification of 1-metallacyclobuta-2,3-dienes: A Case Study of Group 4 Metallocene Complexes*"

The work I undertook is the synthesis of all the complexes and the basic characterization. In addition, a major part of the supporting information corresponding to the paper was written by me, as well as a one-third of the manuscript corresponding to the paper was written by me. Contribution to this paper is 70%.

Publication 4: **Sihan Li**, Mirjam Schröder, Xinzhe Shi, Anke Spannenberg, Jörg Fischer, Björn Corzilius, Fabian Reiß and Torsten Beweries, *submited*.

"*Reactions of group 4 1-metallacyclobuta-2,3-diene complexes with diazenes: N=N bond cleavage vs. N-C bond formation and dearomatization*"

The work I undertook is the synthesis of most of the complexes and the basic characterization. In addition, a major part of the manuscript and supporting information corresponding to the paper was written by me. Contribution to this paper is 80%.

(Torsten Beweries) (Sihan Li)

4.1 1-Zirconacyclobuta-2,3-dienes: synthesis of organometallic analogs of elusive 1,2-cyclobutadiene, unprecedented intramolecular C-H activation, and reactivity studies

Xinzhe Shi, **Sihan Li**, Melanie Reiß, Anke Spannenberg, Thorsten Holtricter-Rößmann, Fabian Reiß and Torsten Beweries.

Chem. Sci. **2021**, *12*, 16074-16084

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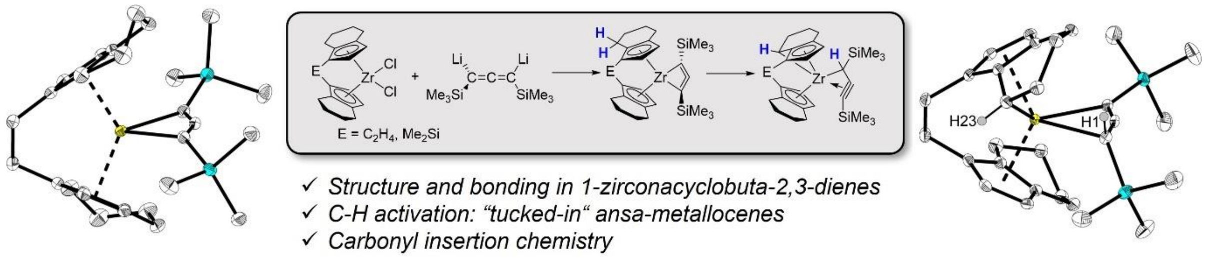
Contribution to this paper is 20%



✓ Structure and bonding in 1-zirconacyclobuta-2,3-dienes
✓ C-H activation: "tucked-in" ansa-metallocenes
✓ Carbonyl insertion chemistry

Chemical Science

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1-Zirconacyclobuta-2,3-dienes: synthesis of organometallic analogs of elusive 1,2-cyclobutadiene, unprecedented intramolecular C–H activation, and reactivity studies†

Xinzhe Shi,[a] Sihan Li,[a] Melanie Reiß,[a] Anke Spannenberg,[a] Thorsten Holtrichter-Rößmann,[b] Fabian Reiß *[a] and Torsten Beweries *[a]

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The structure, bonding, and reactivity of small, highly unsaturated ring systems is of fundamental interest for inorganic and organic chemistry. Four-membered metallacyclobuta-2,3-dienes, also referred to as metallacycloallenes, are among the most exotic examples for ring systems as these represent organometallic analogs of 1,2-cyclobutadiene, the smallest cyclic allene. Herein, the synthesis of the first examples of 1-zirconacyclobuta-2,3-dienes of the type [$Cp'_2Zr(Me_3SiC_3SiMe_3)$] (Cp'_2 = *rac*-(ebthi), (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) (**2a**); *rac*-$Me_2Si(thi)_2$, thi = (η^5-tetrahydroindenyl), (**2b**)) is presented. Both complexes undergo selective thermal C–H activation at the 7-position of the *ansa*-cyclopentadienyl ligand to produce a new type of "tucked-in" zirconocene system, **3a** and **3b**, that possesses a η^3-propargyl/allenyl ligand. Both types of complexes react with carbonyl compounds, producing enynes in the case of **2a** and **2b**, as well as η^1-allenyl complexes for **3a** and **3b**. Computational analysis of the structure and bonding of **2a** and **3a** reveals significant differences to a previously described related Ti complex. All complexes were fully characterised, including X-ray crystallography and experimental results were supported by DFT analysis.

Introduction

Organometallic complexes of early transition metals show great potential for a variety of unusual bond activation reactions and for the stabilisation of exotic bond situations.[1] In this context the study of formation and reactivity of unsaturated, unusual five-membered metallacycles such as 1-metallacyclopent-3-ynes,[2] 1-metallacyclopenta-2,3,4-trienes[3] or 1-metallacyclopenta-2,3-dienes[4] has attracted great attention in the past. In these molecules, the metal centre plays an important role for the stability of the seemingly abnormal cyclic geometries, interacting with the central double or triple bond of the metallacyle.[5] In general, the chemistry of highly strained metallacycles is of particular interest to realise unusual bonding situations that can pave the way to new types of ligand architectures or new chemical transformations. A recent example was reported by Tonks, Goodpaster, Copéret and co-workers, who showed that carbodiimide coordination at $Cp_2Ti(II)$ (Cp = η^5-cyclopentadienyl)[6] results in the formation of a strained 4-membered nitrogen-containing metallacycle bearing a free carbene.[7]

In recent years, we became interested in the synthesis of even smaller highly unsaturated four-membered all-carbon metallacycles and computationally evaluated the possibilities of accessing such structures.[8] In the past, group 5 metallacyclobutadiene complexes have been reported as intermediates and deactivation products in alkyne metathesis.[9–11] Following up on several unsuccessful approaches, such as attempted coupling of alkynyl and isocyanide ligands at Ti(III),[12] or deprotonation of a promising propyne precursor,[13] we have presented the synthesis and isolation of a dilithiated allene synthon [$Li_2(Me_3SiC_3SiMe_3)$] (**1**) that could furnish the desired 1-metallacyclobuta-2,3-diene complexes in a simple salt metathesis reaction with metallocene dihalide.[14a] However, in reactions with [Cp_2ZrCl_2] and [Cp_2HfCl_2] only dinuclear, allenediide bridged metallocene complexes could be obtained (Fig. 1a).[14]

Recently reactions of the *ansa*-titanocene [*rac*-(ebthi)$TiCl_2$] (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with **1** resulted in the formation of the unusual metallacycle **A** (Fig. 1b).[15] This compound is best described as an unusual biradicaloid system, possessing a formal Ti(III) centre that is antiferromagnetically coupled with a monoanionic radical

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† Electronic supplementary information (ESI) available. CCDC 2113148–2113157. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc06052j

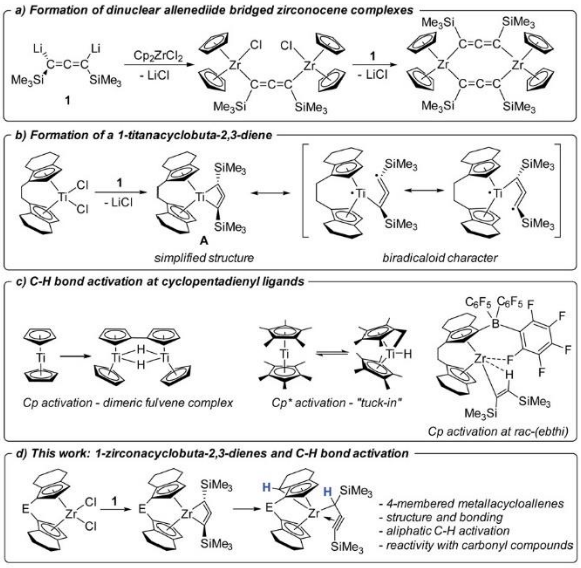


Fig. 1 Contextualisation of the present work.

ligand. First studies of the reactivity showed that **A** selectively reacts with ketones and aldehydes to yield enynes by oxygen transfer to titanium.

Bridged *ansa*-metallocenes such as *rac*-(ebthi)M (M = Ti, Zr, Hf) were first developed by Brintzinger[16] and were found to show excellent performance in the stereospecific synthesis of polyolefins.[17] Additionally these and related systems were used as catalysts for a variety of stereoselective synthetic applications.[18] Activation reactions of the metallocene framework that result in deactivation of the catalyst or could open pathways for undesired side-reactions are typically not considered. In the organometallic chemistry of group 4 metallocenes, intramolecular aliphatic C–H activations at non-Cp containing alkyl groups have been reported before.[19] C–H activation reactions at the metallocene fragment include the well-studied case of Cp* (Cp* = η^5-C_5Me_5) "tuck(ed)-in"[20], for example, forming a hydride complex [(Cp*)($C_5Me_4CH_2$)TiH] from [$Cp*_2Ti$] (Fig. 1c). The aromatic C–H activation at Cp ligands is rather uncommon, although a classical example has been described for titanium, where free "titanocene" is in fact the doubly C–H activated dimeric species [((Cp)(C_5H_4)TiH)$_2$].[21] In 2003 Rosenthal reported an unusual aromatic C–H activation of the *rac*-(ebthi) ligand at Zr in the presence of the Lewis acid [$B(C_6F_5)_3$] (Fig. 1c).[22] In addition, intermolecular C–H activation reactions are involved as key steps in the activation and coupling of small molecules at Ti and Zr complexes.[23]

In this contribution, we present the synthesis and characterisation of two Zr analogs of the Ti complex **A** as well as their transformation into unprecedented aliphatic C–H activation products (Fig. 1d). Furthermore, the reactivity of these complexes with carbonyl compounds is discussed in comparison with the Ti system. Finally, we attempt to rationalise the selective formation of metallacycles for the herein described examples and discuss this in the context of previous work on related zirconocenes.

Results and discussion

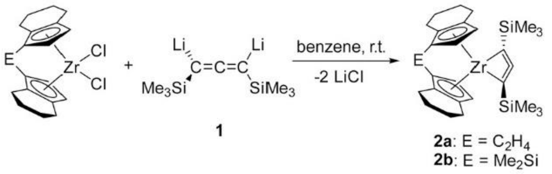
Synthesis and characterisation of 1-zirconacyclobuta-2,3-dienes

Reaction of [*rac*-(ebthi)$ZrCl_2$] and the dilithiated allene **1** at room temperature in non-polar solvents such as benzene or toluene furnishes complex **2a**, the zirconocene analog of the previously described Ti complex **A** (Scheme 1). Similarly, the reaction of the dimethylsilyl bridged complex [$Me_2Si(thi)_2ZrCl_2$] (thi = η^5-tetrahydroindenyl) with **1** furnishes the corresponding complex **2b**. Both complexes were characterised by NMR spectroscopy and their ^1H NMR spectra show informative doublet resonances which correspond to the Cp protons (**2a**: *d* 7.20, 5.35, **2b**: *d* 7.43, 5.40 ppm). In ^{13}C NMR spectra, the signals of the metal bound C atoms of the formal allene unit are observed at 164.7 (**2a**) and 173.2 ppm (**2b**), whereas the internal C atoms resonate at higher field (**2a**: 151.4, **2b**: 147.0 ppm). Compared to the previously described Ti complex **A**, the metal bound C atoms of the two Zr complexes **2a** and **2b** resonate at much higher field (Ti–*C* 213.8 ppm), while the signals of internal C atoms were found at lower field than for **A** (C=*C*=C 134.2 ppm), indicating significant differences in the electronic structures.

X-ray analysis of single crystals of complexes **2a** and **2b** that were obtained by storing the concentrated pentane solution at −30 °C (Fig. 2) shows the corresponding Zr centre in distorted tetrahedral coordination geometry with the bridged cyclopentadienyl ligand and the allenediide ligand. Based on the experimental bond parameters, these complexes are best described as a Zr(IV) species with a covalently bound dianionic allenediide ligand (**2a**: Zr1–C1 2.3099(12), Zr1–C3 2.3074(12), C1–C2 1.3100(18), C2–C3 1.3076(18) Å, C1–C2–C3 149.32(12)°; **2b**: Zr1–C1 2.342(4), Zr1–C3 2.319(4), C1–C2 1.302(6), C2–C3 1.290(5) Å, C1–C2–C3 150.5(4)°; $\Sigma r_{\mathrm{cov,Zr-C}} = 2.29$, $\Sigma r_{\mathrm{cov,C=C}} = 1.34$ Å [24]). Notably, while the latter values are identical in the Ti system, metal-carbon bonds are well in line with Zr–C single bonds in this case, whereas for **A**, much longer Ti–C distances were observed. This could be explained by the well-known greater bond strength of metal–ligand bonds for 4d compared to 3d metal systems and could point to pronounced differences in stability and reactivity (*vide infra*).

Intramolecular aliphatic C–H bond activation

Interestingly, in solution, complex **2a** undergoes a selective intramolecular C–H bond activation of the CH_2 group in the 7-position of the 4,5,6,7-tetrahydroindenyl moiety to furnish a propargyl complex **3a** (Scheme 2). The nature of the thus



Scheme 1 Synthesis of 1-zirconacyclobuta-2,3-diene complexes **2a** and **2b**.

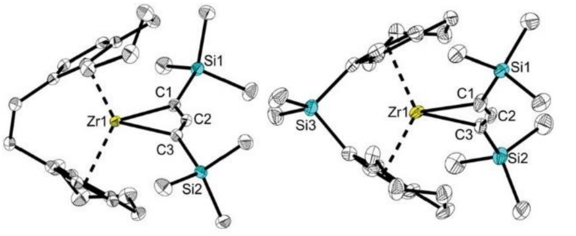


Fig. 2 Molecular structure of complexes **2a** (left) and **2b** (right). Thermal ellipsoids correspond to 30% probability. Hydrogen atoms and the second position of the disordered tetrahydroindenyl group are omitted for clarity.

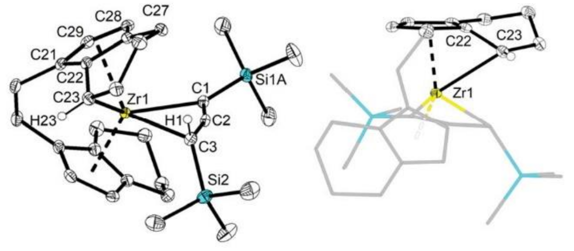
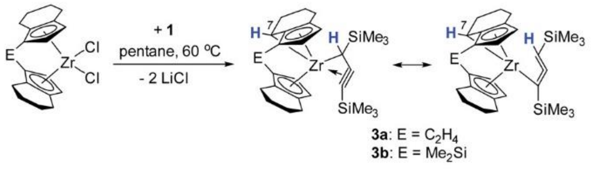


Fig. 3 Left: molecular structure of complex **3a**. Right: alternative view of complex **3a**, illustrating the presence of a covalent bond between Zr1 and C–H activated C23. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms (except H1 and H23), solvent molecule and the second position of the disordered tetrahydroindenyl and $SiMe_3$ group are omitted for clarity. Selected bond lengths and angles for **3a**: C1–C2 1.262(3), C2–C3 1.364(3), C21–C29 1.419(3), C21–C22 1.439(3), C22–C27 1.439(2), C27–C28 1.403(3), C28–C29 1.409(3), C22–C23 1.420(3), C1–Zr1 2.4407(18), C2–Zr1 2.3924(17), C3–Zr1 2.5747(18) Å; Zr1–C1–C2 72.76(11), C1–C2–C3 158.56(18), C2–C3–Zr1 66.81(10), C1–Zr1–C3 61.86(6)°, $\Sigma(\angle C22) = 350°$.

formed metallocene fragment is strongly reminiscent of so-called "tucked-in" complexes that are commonly observed for Cp* ligands.[25] Notably, this mode of ligand activation has not been observed to date for this type of *ansa*-cyclopentadienyl ligands. This process occurs slowly at room temperature. To facilitate this transformation, we increased the temperature to 60 °C, and found that the reaction of [*rac*-(ebthi)$ZrCl_2$] with the dilithiated allene **1** in pentane or benzene generates this Zr propargyl complex **3a** with full conversion after four days. The colour of the reaction solution turned from greenish to brown at last. A similar dimethylsilyl bridged C–H bond activation product **3b** can be obtained from **2b**, albeit in much less reaction time of only one day.

The ^1H NMR spectra show five doublet resonances at δ 5.75, 5.72, 5.48, 5.43 and 4.23 ppm for **3a**, and δ 5.86, 5.74, 5.62, 5.35 and 3.79 ppm for **3b**, corresponding to the CH protons of cyclopentadienyl and fused cyclohexyl groups of the metallocene moiety. The ^{13}C NMR spectra show three characteristic signals which are assigned to the terminal ($C{\equiv}\mathit{C}{-}SiMe_3$, **3a:** 141.9, **3b:** 139.3 ppm), internal ($\mathit{C}{\equiv}C{-}SiMe_3$, **3a:** 96.2, **3b:** 96.3 ppm) and metal bound carbon atoms (Zr–*C*, **3a:** 51.5 ppm, **3b:** 51.4 ppm) of the propargyl unit.

Single crystals of these unusual species **3a** and **3b** could be obtained from concentrated benzene solution at room temperature. The molecular structure of complex **3a**[26] (Fig. 3, left) reveals the presence of a Zr propargyl complex as a four-membered ring system. Early transition metal complexes with $CH_2C{\equiv}CR$ units are known as the combination of η^3-propargyl and η^3-allenyl resonance structures.[27] In the herein reported $CH(SiMe_3)C{\equiv}CR$ structure, C1–C2 and C2–C3 bond lengths correspond to a triple and double bond, respectively, and the C_3 ligand unit is thus best described as a resonance form between η^3-propargyl and allenyl structures. The Zr–C1–C2–C3 unit is planar (−1.5(5)°) and this is also in agreement with the planarity of such η^3-propargyl/allenyl complexes. Contacts to the activated fragment of the former *rac*-(ebthi) ligand are 2.141 (Zr-$Cp'_{centroid}$) and 2.5703(18) Å (Zr1–C23). Although the latter value is considerably larger than in Bouwkamp's [$Cp^*(\eta^6$-$C_5Me_4CH_2)Zr(thf)]^+$ (**B**) (2.366(4) Å)[28] and Marks' [$Cp^*(\eta^6$-$C_5Me_4CH_2)ZrPh$] (**C**) (2.388(7) Å),[29] the deviation from planarity at C22 (Fig. 3, right; $\Sigma\angle(C22; \mathbf{3a}) = 350°$; $\Sigma\angle(C115; \mathbf{B}) = 346°$; $\Sigma\angle(C1; \mathbf{C})$ 346°) clearly indicates the presence of a η^5,η^1 (or η^6)-bound fragment. Taken together, one C23–H bond is intramolecularly activated and the proton is transferred to the C_3 ligand, resulting in an unusual formally trianionic, bridged tucked-in metallocene structure (Fig. 3, right) that possesses a η^3-propargyl/allenyl unit coordinated to the Zr centre. As mentioned above, slow transformation of 1-metallacyclobuta-2,3-dienes **2a** and **2b** in solution yielded C–H bond activation products **3a** and **3b** with high conversion (**3a**: 88%, **3b**: 98%) after weeks at room temperature (Fig. 4). However, 10% of residual **2a** was obtained from the solution of **3a** after one month, which is not the case for **3b** (Fig. S19†). In addition, the mutual interconversion between these two species **2** and **3** at room temperature can explain why pure NMR spectra of compounds **2a**, **2b**, and **3a** are generally not possible to obtain. A similar, fast and selective C–H activation reaction was not observed using Ti complex **A**, however, slow conversion into a hitherto unidentified species takes place at 60 °C (Fig. S21†).



Scheme 2 Synthesis of C–H bond activation products **3a** and **3b**.

To obtain further insights into this unusual C–H activation sequence, we have analysed this process for the system **2a**/**3a** computationally using a stepwise approach where we first identified an appropriate reaction path using a smaller double zeta basis set, followed by using a more sophisticated triple zeta basis set. All geometries were optimised and were confirmed to be local minima or first order saddle points (for transition states, TS) on the potential energy surface by harmonic vibration frequency calculation on the same level of theory (B3LYP[31]/GD3BJ[32]/(def2svpp)def2tzvp[33]). We were intrigued by the selective formation of complexes **3a** and **3b** where only one CH_2 group of the tetrahydroindenyl fragment is activated and

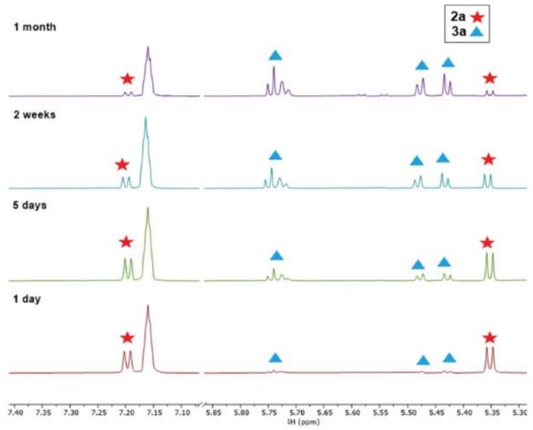


Fig. 4 ^{1}H NMR spectroscopic monitoring of the transformation of **2a** to **3a** (25 °C, benzene-d_6, 300.2 MHz, low-field region, δ 7.07–5.87 ppm are omitted for clarity).

a proton is shifted to the metal coordinated C_3 unit. Therefore, we first calculated the Gibbs free energies for the activation of all five CH_2 groups present in the *rac*-(ebthi) ligand as well as their TS (Fig. 5). These calculations nicely show that only the formation of the experimentally found isomer 1 is exergonic ($\Delta_R G = -0.2$ kJ mol^{-1}). However, the TS to produce isomer 4 ($\Delta_R G = 112.8$ kJ mol^{-1}) is significantly lower in energy than that for isomer 1 ($\Delta_R G = 138.7$ kJ mol^{-1}). We have thus next analysed two possible paths of subsequent H migration from isomer 4 to isomer 1 and found that neither the migration of the outer (*exo*) CH protons nor that of the protons facing the metal (*endo*) show TS which would support this concept (all TS >250 kJ mol^{-1}, Fig. 5a and Table S6†). As consequence, direct C–H activation was evaluated using the larger basis set def2tzvp (Fig. 5b and Table S7†). These calculations confirm isomer 1 as the thermodynamically preferred product of the reaction. Interestingly, the TS for its formation ($\Delta_R G = 102.6$ kJ mol^{-1}) now also is lowest in energy and even allows a C–H activation reaction at room temperature. This nicely confirms the experimentally observed formation of complex **3a** from **2a** within days (Fig. 4). The minor calculated energy difference between **2a** and **3a** of only -0.75 kJ mol^{-1} suggests the feasibility of the inverse reaction in which **2a** is formed from **3a**. The equilibrium composition at room temperature estimated using the Bolzmann distribution theorem is 42/58% (**2a**/**3a**). In line with this, ^{1}H NMR monitoring of solutions of complex **3a** over one month shows slow, but constant conversion to produce the 1-metallacyclobuta-2,3-diene **2a** (Fig. S16†).

Computational analysis of structure and bonding in complexes 2 and 3

As mentioned above, the Ti compound **A** can be described as an unusual antiferromagnetically coupled biradicaloid system, possessing a formal Ti(III) centre coordinated with a monoanionic alleneylide ligand. In that case, Complete Active Space (CAS(8,9)) SCF calculations, determined a biradical character of $\beta = 28\%$. To compare the bonding situation of the Zr analog **2a** we first evaluated the stability of the Kohn–Sham wavefunction from B3LYP calculation and found that this is stable. However, the Hartree–Fock wavefunction shows an RHF/UHF instability for **2a**, the same was observed in **A**, but not for complex **3a**. Therefore, we investigated the electronic situation of **2a** as an open-shell singlet considering similar CAS molecular orbitals (MOs) as for **A** (Fig. S121†). This calculation reveals a negligible occupation number in the formal LUMO (ϕ_5) orbital of only 0.08 electrons. Even though we also found a lower biradicaloid character in a previous study of zirconocene phosphinidenes compared to its titanocene analogs, this finding was surprising.[34] Based on this result we neglect the biradicaloid

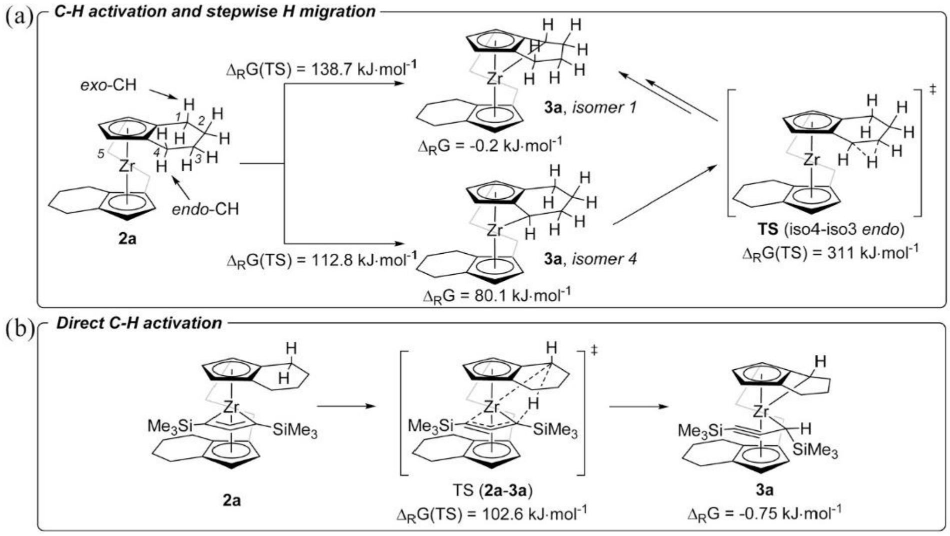


Fig. 5 (a) Hypothetical formation of **3a** from **2a** *via* C–H activation and stepwise H migration. For clarity, complexes **2a** and **3a** are shown without the C_3 ligand (B3LYP/GD3BJ/def2svpp). (b) Direct C–H activation to produce **3a** (B3LYP/GD3BJ/def2tzvp).[30]

character of **2a** and **2b.** We next evaluated the contour plots of the Laplacians of the electron density $\nabla^2 r$ of the investigated complexes and overlaid these with the results from the quantum theory of atom in molecules (QT-AIM) analysis[35] and their Wiberg bond indices (WBIs, given in italics) (Fig. 6 and S112–S114†). The QT-AIM analysis of related group 4 1-metallacyclobuta-2,3-diene complexes **2a**, **2b**, and **A** revealed two M–C "bond" paths in the metallacycles in between the metal centre and the α-carbon atoms, respectively (**2a**: Fig. 6 left; **2b**: Fig. S113;† **A**: Fig. S114†). Ring critical points were located between the metal centre and the β-carbon atom, thus indicating the absence of a bonding interaction between the central carbon atom and the metal centre. The lower WBI between the central carbon atom and the metal centre compared to the α-C–M bonds nicely supports the findings of the QT-AIM analysis. Furthermore, the value of 1.95 for the C–C bonds in the allene units in **2a** and **2b** clearly reveals these as double bonds based on this theory (*cf.* 1.93 in **A**). For η^3-propargyl/allenyl complexes **3a** and **3b** (**3a**: Fig. 6 right; **3b**: Fig. S116†) the QT-AIM analysis shows only one "bond" path between the $Me_3SiCCCHSiMe_3$ unit and the Zr centre. The WBI of these bonds are lower than 0.6 but these values are larger than those of the other M–C interactions, which supports the QT-AIM analysis. In line with the description as η^3-propargyl/allenyl complexes two different WBI could be determined along the C_3 unit (1.7 and 2.2) in both complexes. Furthermore, the additional analysis of the natural bond orbitals (NBO)[36] and the investigation of the natural localised molecular orbitals (NLMO) of complexes **2a**, **2b** and **3a** confirm the previous results (see ESI,† section 8.3.1). The analysis of the NLMOs reveals small contributions (7.4–2.3%) of a d orbital at Zr for the allene CC π-type orbitals. These are absent for the corresponding CC σ-type orbitals. This additional interaction could contribute to the stabilisation of the four-membered ring systems studied here. Since the Laplacian plots indicate a polarised α-C–M bond, we finally summed the natural charges (NBO) of all atoms in the $Me_3SiCCCSiMe_3$ fragments which shows significantly larger values for the Zr complexes **2a** and **2b** compared to its lighter congener **A** (**2a:** −0.98; **2b:** −0.95; **A:** −0.74). This points to a higher polarity of the M–C interaction in the zirconacycles **2a** and **2b** and is well in line with the greater biradicaloid character of the Ti complex **A.** This difference should affect the reactivity of the here investigated Zr complexes compared to that of **A.**

Reactivity of 1-metallacyclobuta-2,3-dienes 2a/2b and propargyl/allenyl complexes 3a/3b

Before investigating the reactivity of complexes of types **2** and **3**, we first evaluated their stability upon exposure to air or water. Unsurprisingly, in both cases, formation of the well-known propyne $Me_3SiC{\equiv}CCH_2SiMe_3$ was observed[14,37] which is in line with observations made for Ti complex **A** (Fig. S14, S15, S17 and S18†).

As mentioned above, the Ti complex **A** shows well-defined reactivity with carbonyl compounds, producing enynes[38] by coupling of the allenediide fragment with the methylene unit of the substrate and oxygen transfer to the Ti centre. In general, reactions of unsaturated substrates with C = X (X = heteroatom) moieties are well-studied for a variety of group 4 metallacycles and 1,2- or 2,1-insertions are commonly observed.[39] Reactions of complexes **2a** and **2b** with benzophenone, acetophenone and acetone showed similar reactivities as **A** to furnish corresponding enynes **5**, **7**, and **9** as the final product (Scheme 3).

However, unlike **A** which shows full conversion within 16 hours at room temperature, Zr complexes of type **2** required longer time at room temperature or harsher reaction conditions to produce enynes (see ESI† for details). It should be noted that after adding ketones into the solution of complex **2a** at room temperature, the colour of the solution changed from green to orange immediately. To our delight, single crystals of complexes **4** and **6** could be obtained from *n*-hexane and confirmed the assignment as a six-membered ring system, formed by insertion of ketone into

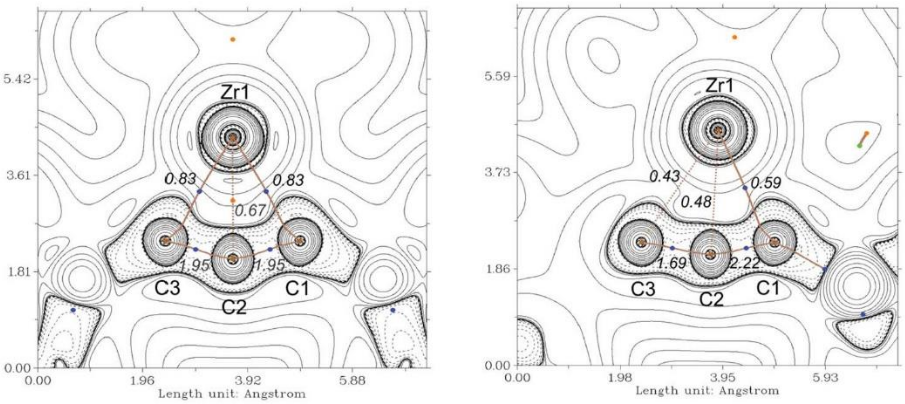
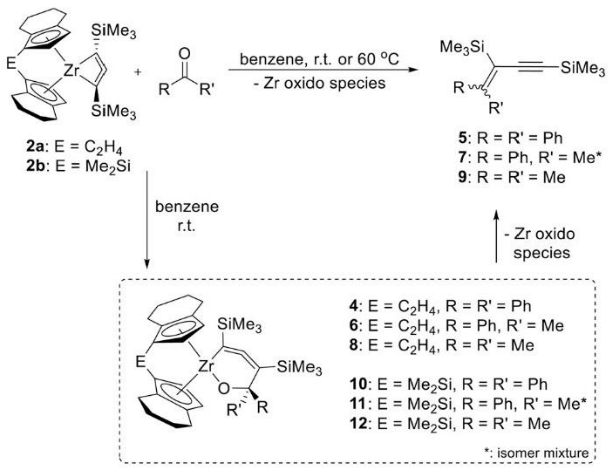


Fig. 6 Contour plots of the Laplacians of the electron density $\nabla^2 r$ of complexes **2a** (left) and **3a** (right) in the C–Zr–C plane. Dashed lines indicate negative (local charge concentration), solid lines indicate positive values (local charge depletion). The Laplacian plot is overlaid with the molecular graph from QT-AIM analysis and Wiberg bond indices (italic small numbers). Brown lines indicate bond paths, brown dashed lines are hyphothetical bonds, blue dots correspond to bond critical points, light brown dots indicate ring critical points. Density from B3LYP/GD3BJ/def2tzvp.



Scheme 3 Reaction of complexes **2a** and **2b** with ketones to yield enynes **5**, **7** and **9**. Note: compound **4** contains compound **13** (*vide infra*) as an impurity as **2a**, used for its synthesis always contains traces of **3a** (Fig. S43†).

the Zr–C bond of the 1-metallacyclobutadi-2,3-ene.[40] In compound **6** (Fig. 7), C1–C2 (1.2951(19) Å) is shorter than C2–C3 (1.3398(19) Å), however, both distances correspond to double bonds. The Zr1–C1 distance of 2.3172(13) Å is slightly longer than typical single bonds, while the Zr1–C2 and Zr1–C3 distances are 2.5083(13) Å and 3.0433(14) Å, respectively, as the result of the ring enlargement. Release of ring strain, compared to **2a**, thus leads to substantial linearisation of the allene unit (C1–C2–C3 166.5(2)°). The Zr1–O1 distance of 2.0362(9) Å indicates the presence of a shortened Zr–O single bond ($\Sigma r_{\text{cov,Zr–O}} = 2.17$ Å [24]) that is slightly longer than found in related complexes formed by insertion of carbonyl compounds.[41]

Without workup, the orange residue of **8** was analysed by NMR spectroscopy. The ^{1}H NMR spectrum showed four doublet resonances at δ 6.68, 6.43, 5.43 and 5.18 ppm, corresponding to the Cp protons of a new metallacyclic species, formed by a similar insertion of acetone.

The reactions of related **2b** with ketones were performed in benzene-d_6 in Young-NMR tubes. Corresponding intermediates (**10**, **11** or **12**) and the same final enynes (**5**, **7** or **9**) could be clearly identified by ^{1}H NMR spectroscopy without further workup. These observations are well in line with the calculated Gibbs free energies of this reaction sequence, which indicate that formation of the six-membered ring systems is exergonic in all cases (range: $\Delta_R G = -101.32$ (**6**); -114.52 (**10**) kJ mol^{-1}). The subsequent formation of the enynes **5**, **7**, and **9** as the final products is endergonic with respect to these insertion products, but still overall exergonic (Tables S8 and S9†). Similar intermediates of reactions of **A** were calculated to be endergonic, which explains why we could isolate these insertion products only for the herein described Zr systems.

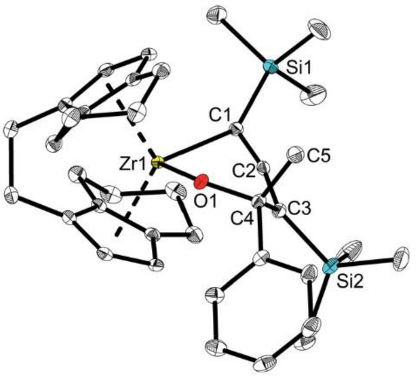
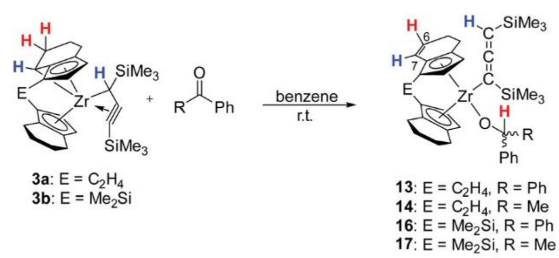


Fig. 7 Molecular structure of complex **6**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

Reactions of ketones with five-membered all-C-metallacycloallenes were investigated before, however, isolation of the organometallic species, formed by 1,2-insertion was not reported.[4e] Formation of heterometallacycles, either by insertion into the M–C bond or through cycloaddition, followed by redox-neutral[42] or reductive cleavage[43] of the newly formed metallacycles, is common for group 4 complexes and its utility for organic synthesis was demonstrated on various occasions.

Tucked-in complexes show a rich organometallic chemistry that is dominated by insertion reactions into the metal–carbon bond.[44] The reactivity of complexes **3a** and **3b** was investigated with benzophenone or acetophenone at room temperature. After one day a new Zr(IV) complex was obtained which contains an alcoholate group covalently bound to Zr and possesses a η^5-4,5-dihydroindenyl fragment, *i.e.* a doubly C–H activated six-membered ring of a former *rac*-(ebthi) ligand (Scheme 4). Notably, no organic products were detected after four days at 80 °C. The ^{1}H NMR spectrum of complex **14** as an example shows four doublet resonances (δ 6.47, 5.53, 5.44 and 5.08 ppm), one quartet resonance (δ 5.28 ppm) and one singlet resonance (δ 3.30 ppm), which are consistent with the presence of Cp, alcoholate and allene groups. Besides, the two protons at 6- and 7-position of the former indenyl ring were found at 6.41 and 5.69 ppm, which was confirmed by ^{1}H,^{1}H COSY and NOESY experiments. In ^{13}C NMR spectra, three characteristic signals are assigned to the internal C atom (195.5 ppm), metal-bound (101.1 ppm) and terminal C atom (51.9 ppm) of the C_3 unit, whereas the signal for the O bound C atom is observed at 81.8 ppm.

Single crystals of **13** and **14** obtained from *n*-hexane unequivocally clarified the above-made structural assignment.[40] The molecular structure of complex **14** (Fig. 8) shows the bent



Scheme 4 Reaction of **3** with benzophenone/acetophenone to yield **13**, **14**, **16** and **17**.

metallocene coordinated with a covalently bound alcoholate ligand and monoanionic allenyl ligand. In line with an η^1-allenyl/propargyl resonance C1–C2 (1.2924(17) Å) is slightly shorter than C2–C3(1.3257(18) Å) and both bond lengths are in the range of shortened double bonds. The angle C1–C2–C3 is 179.29(14)°, which shows the linear arrangement of allene. Although the molecular structure of complex **14** shows disorder, the C35A-C36A distance (1.336(4) Å) in the six-membered ring of the former *rac*-(ebthi) ligand is consistent with typical C=C bond.[45]

While *rac*-(ebthi), *rac*-(ebi) (ebi = 1,2-ethylene-1,1′-bis(η^5-indenyl)) and related η^5-indenyl complexes of group 4 metals are frequently used,[46] especially in polyolefin chemistry,[47] examples for well-defined complexes possessing 4,5-dihydroindenyl moieties as part of the metallocene fragment are elusive and to the best of our knowledge were not isolated and characterised before. Such species can be regarded as intermediates for industrially relevant hydrogenation of [*rac*-(ebi)ZrCl$_2$] to produce [*rac*-(ebthi)ZrCl$_2$].[48] Furthermore, complexes **13**, **14**, **16**, and **17** represent rare examples for stable η^1-allenyl complexes as such species tend to be in equilibrium with η^1-propargyl complexes.[27g] We would further like to mention that these complexes result from a formal hydride transfer from the formally trianionic tucked-in ligands to the ketone substrate.

Interestingly, complexes **3a** and **3b** showed a different reactivity in the reaction with acetone. When performing the reaction at room temperature, no desired organometallic product was identified by NMR spectroscopy. While monitoring the reaction with two equivalents of acetone at 80 °C, we observed the formation of a major product (Scheme 5) resulting from the insertion of the C=O bond of acetone into the Zr–C bond of the activated C$_3$ ligand.

The ^{1}H NMR spectrum of the organic product that was obtained after purification by column chromatography shows two singlet resonances at δ 1.52 (broad) and 1.97 ppm, corresponding to protons of a hydroxyl group and a methine group.

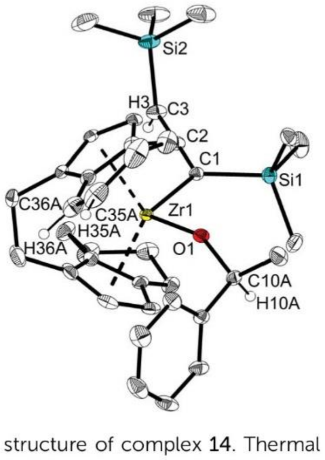
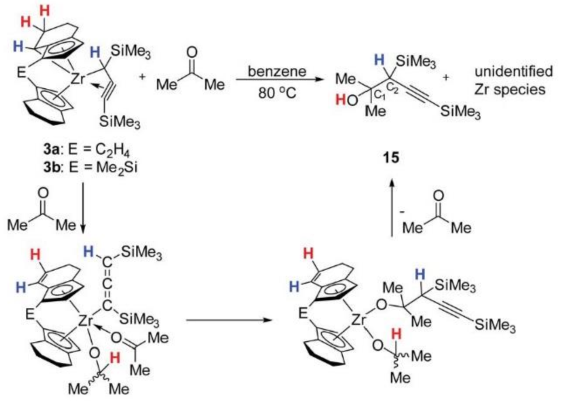
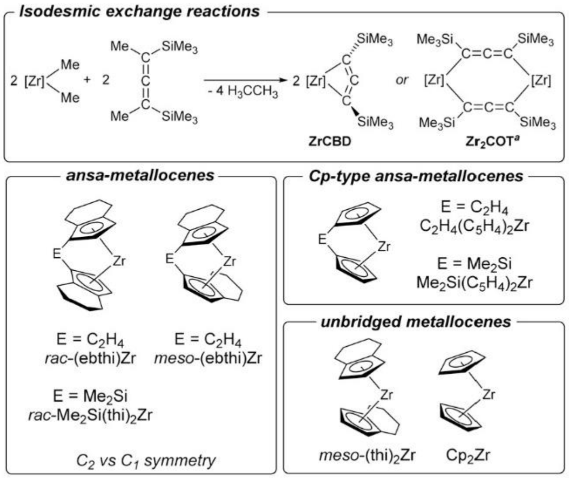


Fig. 8 Molecular structure of complex **14**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms (except H3, H10A, H35A and H36A) and the second position of the disordered group are omitted for clarity.



Scheme 5 Reaction of **3** with acetone to yield **15** and postulated mechanism for the insertion of acetone and product formation.

The ^{13}C NMR spectrum showed two resonances due to the alkynyl group at 108.4 and 88.2 ppm, while the signals at 72.5, 0.4 and −0.5 ppm suggested the presence of proton-free C atom C$_1$ and SiMe$_3$ groups. The IR spectrum shows a band at $\nu = 3463$ cm^{-1} for the OH group (Fig. S107†). MS analysis shows fragments at *m*/*z* 186 [M–CMe$_2$OH$^+$], 152 [M–OH–TMS$^+$], 147 [M–C=CTMS$^+$] and 137 [M–OH–Me–TMS$^+$] that supports the assignment as an alcohol containing an alkynyl group (**15**). Based on literature precedent, we postulate that compound **15** forms *via* a η^1-allenyl complex that is similar to those shown in Scheme 4. Interaction of ketone with the metal centre of the allenyl complex, followed by insertion of the ketone into the Zr–C bond and rearrangement could produce a bis(alkoxide) species. Intramolecular protonation would result in the formation of product **15** (Scheme 5). Related reactivity was described for a titanocene system.[49]



Scheme 6 Top: computed isodesmic exchange reactions to evaluate the thermodynamics of formation of dinuclear complexes *vs.* that of 1-zirconacyclobuta-2,3-diene. Bottom: metallocene fragments used for the above calculations. ^{a}Formation of **Zr$_2$COT** is known to occur *via* the dinuclear allenediide bridged chloride complex [Zr](Cl)(Me$_3$SiC$_3$-SiMe$_3$)[Zr](Cl) (**Zr$_2$Cl$_2$**) (*cf.* Fig. 1a).

Table 1 Computed Gibbs free energies and reaction enthalpies (in kJ mol^{-1}) for hypothetical 1-zirconacyclobuta-2,3-dienes (**ZrCBD**) and dinuclear complexes (**Zr_2COT**). B3LYP/GD3BJ/def2svpp

Entry	[Zr]	$2 \times \Delta H$(**ZrCBD**)	$2 \times \Delta G$(**ZrCBD**)	ΔH(**Zr_2COT**)	ΔG(**Zr_2COT**)	$\Delta\Delta H^a$	$\Delta\Delta G^a$
1	*rac*-(ebthi)Zr	−53.22	−106.96	−137.42	−90.92	−84.2	16.04
2	*rac*-$Me_2Si(thi)_2Zr$	−50.01	−99.17	−158.48	−117.81	−108.47	−18.64
3	*meso*-(ebthi)Zr	25.77	−25.95	−148.08	−115.35	−173.85	−89.40
4	$C_2H_4(C_5H_4)_2Zr$	−0.27	−48.95	−295.43	−260.22	−295.16	−211.27
5	$Me_2Si(C_5H_4)_2Zr$	7.59	−45.86	−291.19	−253.85	−298.78	−208.00
6	Cp_2Zr	13.03	−30.30	−277.63	−239.16	−290.66	−208.86
7	*meso*-$(thi)_2Zr$	34.06	−19.62	−188.37	−149.15	−222.43	−129.52

[a] $\Delta\Delta G = \Delta G(\mathbf{Zr_2COT}) - (2 \times \Delta G(\mathbf{ZrCBD}))$. $\Delta\Delta H = \Delta H(\mathbf{Zr_2COT}) - (2 \times \Delta H(\mathbf{ZrCBD}))$.

Consideration of selectivity determining factors: formation of 1-zirconacyclobuta-2,3-diene *vs.* dinuclear complex

The herein described formation of complexes **2a** and **2b** contrasts with previous observations for unsubstituted and unbridged zirconocenes where formation of dinuclear dizirconacyclooctatetraene complexes took place exclusively.[14] To rationalise these differences, we have therefore computed the thermodynamic data of putative four-membered metallacyclic (**ZrCBD**) and dinuclear complexes (**Zr_2COT**) using a set of related cyclopentadienyl ligands (Scheme 6 and Table 1).

For all zirconocenes considered, both reaction channels are highly exergonic. However, the difference in Gibbs free energies $\Delta\Delta G$ shows that formation of the corresponding four-membered **ZrCBD** complex (**2a**) is only thermodynamically preferred ($\Delta\Delta G = 16.04$ kJ mol^{-1}) for the *rac*-(ebthi) ligand. For the *rac*-$Me_2Si(thi)_2Zr$ system, which was also investigated experimentally, this value is slightly exergonic, indicating kinetic stabilisation of complex **2b** ($\Delta\Delta G = -18.64$ kJ mol^{-1}). Only for these two species clearly exothermic reaction enthalpies were calculated ($\Delta H = -26.61$ (**2a**); −25.00 (**2b**) kJ mol^{-1}). In consequence, formation of binuclear **ZrCOT** complexes should be strongly preferred for all other cases. Furthermore, Cp-based systems, whether bridged or not, should form **ZrCOT** complexes much more preferentially (Table 1). The presence of an indenyl unit, however, appears to impede the formation of dinuclear complexes. Reactions of the parent unsubstituted cyclopentadienyl systems were reported by us before for M = Zr, Hf and selectively gave dinuclear allenediide bridged zirconocene and hafnocene complexes,[14] in line with the strong thermodynamic preference of these species (Table 1, entry 6).

To further support these assumptions, we have next performed NMR experiments using further zirconocene complexes shown in Scheme 6. In the reaction of non-bridged $[(thi)_2ZrCl_2]$ (thi = η^5-tetrahydroindenyl) (Table 1, entry 7) with an equimolar amount of **1** formation of mixtures of **Zr_2COT** and its dinuclear chloride precursor **Zr_2Cl_2** is evident, as indicated by the presence of two sets of ^1H NMR signals for the cyclopentadienyl and $SiMe_3$ protons (Fig. S79–S84†). Similarly, NMR analysis of the reaction of C_1 symmetric *meso*-$(ebthi)ZrCl_2$ (Table 1, entry 3) with **1** shows resonances that indicate the formation of singly and double allenediide bridged dinuclear complexes **Zr_2Cl_2** and **Zr_2COT** (Fig. S85–S87†). From this mixture, single crystals could be obtained, and an X-ray analysis confirms these as the respective dinuclear Zr chloride complex (Fig. S25†). Finally, the reaction of the Cp type *ansa*-metallocene $[Me_2Si(C_5H_4)_2ZrCl_2]$ (Table 1, entry 5) with **1** resulted in the formation of the **Zr_2Cl_2** complex, which could be confirmed by ^1H NMR spectroscopy and an X-ray analysis (Fig. S26†). Based on these model studies and the consideration of the thermodynamics of these salt metathesis reactions, we thus conclude that both, the presence of a bridging unit and C_2 symmetry of the metallocene halide are essential for the formation of 1-zirconacyclobuta-2,3-dienes. While the former prevents the rotation of the cyclopentadienyl ligands, the latter factor, by minimizing steric strain, forces the Me_3Si groups into *trans* position of the desired four-membered metallacycle.

Conclusions

We have presented the synthesis of two 1-zirconacyclobuta-2,3-dienes, organometallic analogs of the elusive 1,2-cyclobutadiene. Both complexes can be prepared by salt metathesis using an *ansa*-zirconocene dichloride and a 1,3-dilithiated allene precursor. Computational analysis of the structure and bonding in these complexes shows that in contrast to the previously reported Ti analog the biradical character is neglectable. Instead, the Zr complexes are best described as Zr(IV) species that possess a dianionic allenediide ligand. Both, C_2H_4 and Me_2Si bridged metallacycles undergo selective thermal C–H activation at the 7-position of the tetrahydroindenyl fragment to produce a new type of "tucked-in" metallocene complex. This activation mode is known in metallocene chemistry but was previously not reported for well-established *ansa*-cyclopentadienyl ligands. Based on DFT analysis we propose a direct C–H activation *via* deprotonation as the most likely mechanism for this process.

Reactions of 1-zirconacyclobuta-2,3-dienes with ketones occur *via* the formation of six-membered oxa-zirconacycles. Other than reported before for the Ti system, these insertion products can be isolated and only produce the enyne coupling products after longer reaction times or upon heating. Reactions of the tucked-in η^3-propargyl/allenyl complexes with ketones furnish η^1-allenyl complexes in which further C–H activation at the metallocene results in the formation of a hitherto unknown 4,5-dihydroindenyl ligand.

The formation of 1-zirconacyclobuta-2,3-dienes described herein contrasts with previous observations made for the parent Cp_2Zr system where open, dinuclear, allenediide bridged complexes are formed selectively. Computational analysis of model reactions indicates a thermodynamic preference for the formation of four-membered metallacycles for the herein experimentally studied C_2 symmetric tetrahydroindenyl *ansa*-cyclopentadienyl systems. This assumption was confirmed experimentally using selected model systems. In summary, these data help to rationalise the differences in selectivity and will guide further studies directed at the synthesis and reactivity of these and related unusual metallacycles.

Author contributions

X. S., F. R. and T. B. conceived and conceptualised the project. X. S., S. L., M. R. and A. S. performed the experiments and analysed the data. F. R. performed DFT calculations and analysed the data. T. H.-R. provided resources used in this study. T. B. supervised the project and acquired funding. X. S., F. R. and T. B. prepared and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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4.2 Selective 1,2-insertion of carbodiimides and substrate-divergent silyl group migration at 1-metallacyclobuta-2,3-dienes

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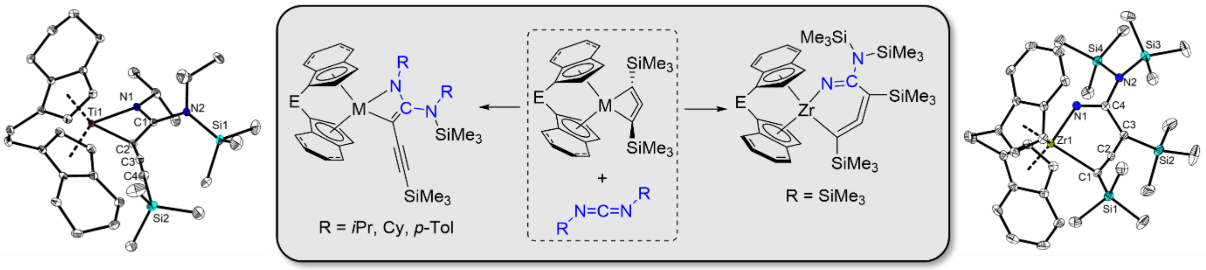

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✓ *17 new aza-metallacycles*
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Selective 1,2-insertion of carbodiimides and substrate-divergent silyl group migration at 1-metallacyclobuta-2,3-dienes†

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The study of new, unusual structures and reactivity patterns is of great interest for various field of organic and organometallic chemistry. Metallacycles of electropositive transition metals represent an excellent platform for this purpose. In this work, we present the synthesis, characterisation, and reactivity toward carbodiimides of a set of ring-strained group 4 *ansa*-metallocene-based 1-metallacyclobuta-2,3-dienes $Cp'_2M(Me_3SiC_3SiMe_3)$ (M = Ti, Zr; Cp′$_2$ = indenyl or tetrahydroindenyl based *ansa*-Cp ligand). In line with experimental studies, computational analysis of the electronic structure of new and previously reported 1-metallacyclobuta-2,3-dienes for the first time shows that the biradical character of these species not only depends on the metal, but also strongly on the nature of the cyclopentadienyl ligands. In reactions with carbodiimides RN═C═NR, depending on the substituents of the carbodiimide, either 2-aza-1-metallacyclobut-3-ene (R = iPr, Cy, and *p*-Tol) or 2-aza-1-metallacyclohexa-2,4,5-triene (R = $SiMe_3$) complexes were produced. Mechanistic studies by DFT calculations reveal that 1,2-insertion of the carbodiimide followed by migration of a $SiMe_3$ group of the metallacycle occurs for R = iPr, Cy, *p*-Tol, whereas for R = $SiMe_3$ insertion is followed by $SiMe_3$ migration along the carbodiimide. The reaction of a 2-aza-1-metallacyclobut-3-ene complex with benzophenone produces a zirconocene amidopyridine complex through a series of unprecedented bond activation and formation events, once again demonstrating the potential of early transition metal complexes for activation and transformation of small molecules.

Introduction

Metallacycles are an important class of metal-based compounds and have found applications in various fields of modern organometallic chemistry, including catalysis,[1] inorganic,[2] organic,[3] and materials chemistry.[4] As an interesting facet of the transformations of metallacycles, transmetallation[5] of its highly functionalised ligands, *e.g.*, to main group compounds, has potential for the synthesis of new metal free cyclic structures that are of interest for a broad range of applications, *e.g.*, in conjugated polymers or as light-emitting materials.[4,6]

Insertion reactivity at the metal–carbon bond of metallacycles is very common and not only key to many catalytic processes such as olefin oligomerisation,[7] but furthermore has the potential to further modify metallacycles formed by simple coupling of unsaturated substrates. More specifically, the coordination, insertion and activation of unsaturated heteroatom containing substrates such as CO_2, carbonyl compounds, nitriles, isocyanides, or carbodiimides can selectively produce new structures with an interesting degree of functionality that may be difficult to access using classical preparative organic techniques and give valuable insights into retrosynthetic pathways aiming at the synthesis of such compounds.[8] For example, nitrile[9] or isocyanide[10] insertion as well as coupling of alkynyl imines[11] readily produces highly functionalised metallacyclic structures. Insertion of carbodiimides into M–C bonds of metallocene alkyne complexes resulted in the formation of five-membered aza-metallacycles (Fig. 1a).[12] This reactivity is strongly dependent on the group 4 metal and the carbodiimide substituents.[13] Products of simple coordination of carbodiimides to a metal centre were isolated[13a] and proposed as intermediates in reactions involving these as sub-

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‡ These authors contributed equally.

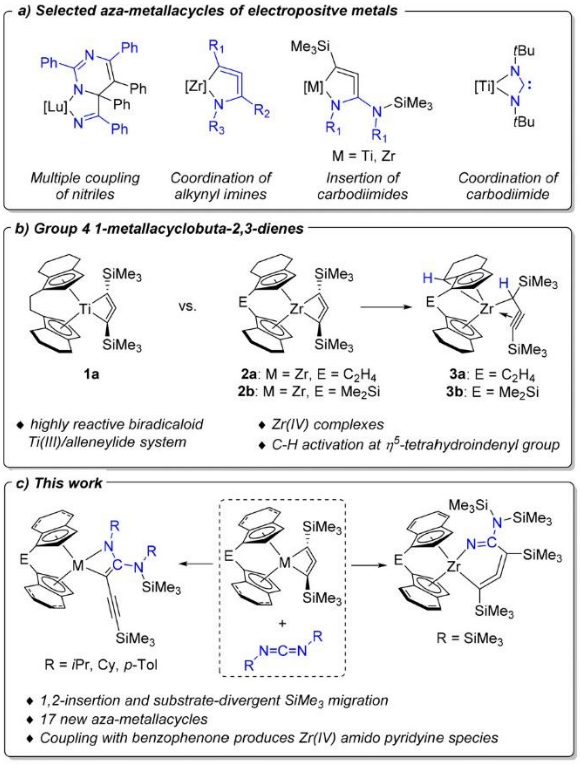


Fig. 1 (a) Selected examples of aza-metallacycles. (b) Group 4 metallacyclobuta-2,3-dienes complexes and C–H activation at η^5-tetrahydroindenyl ligands. (c) Carbodiimide insertion and SiMe$_3$ migration.

strates[14] or products.[15] Metal catalysed functionalisation of carbodiimides such as guanylation[16] or metathesis[17] was reported in the past, involving aza-metallacycles as key-intermediates. In general, aza-metallacycles are an interesting class of organometallic compounds with great potential for the construction of nitrogen containing cyclic and acyclic structures.[18]

Small, ring-strained and highly unsaturated metallacycles have long been elusive,[19] but group 4 metallocenes are a well-suited platform for the realisation of unusual geometries and bond situations. For example, Tonks and co-workers showed that a highly unusual four-membered nitrogen-containing metallacycle bearing a free carbene is accessible by simple carbodiimide coordination at Cp$_2$Ti(II) (Fig. 1a).[13a] We have recently described the synthesis of an all-carbon titanacyclobuta-2,3-diene **1a**, an organometallic analog of the smallest cyclic allene 1,2-cyclobutadiene, by salt metathesis between *rac*-(ebthi)TiCl$_2$ (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) and a dilithiated allene synthon, [Li$_2$(Me$_3$SiC$_3$SiMe$_3$] (Fig. 1b).[20] Complex **1a** displays an unusual electronic situation with considerable biradical character due to the presence of a formal Ti(III) centre that is antiferromagnetically coupled with a monoanionic radical ligand. Following up on this, we have extended these studies to the Zr analogs **2a** and **2b**, which are best described as classical Zr(IV) metallacycles with dianionic C$_3$ ligands (Fig. 1b).[21] In these complexes, selective C–H activation at the *rac*-(ebthi) and *rac*-(sbthi) (sbthi = dimethylsilylene-1,1′-bis(η^5-tetrahydroindenyl)) ligands, respectively, produced a new type of tucked-in Zr(IV) complexes that possesses a η^3-propargyl/allenyl ligand (**3a**/**3b**, Fig. 1b). Although this reaction takes place slowly, the isolation of pure samples of **2a** and **2b** proved to be challenging. Metallacyclobuta-2,3-diene complexes **1a**, **2a**, and **2b** showed insertion reactivity with carbonyl compounds to eventually form enynes through retro-cycloaddition. Notably, oxa-zirconacycles could be isolated as intermediates and fully characterised for **2a** and **2b**.

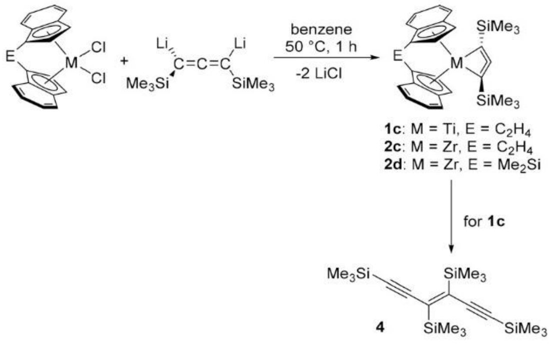
In this contribution, we extend the scope of stable 1-metallacyclobuta-2,3-diene complexes, introducing *ansa*-indenyl-based systems and systematically describe the reactivity of Ti and Zr complexes with a set of carbodiimides, leading to insertion of the heteroallene into the metal–carbon bonds of the metallacycle. Differences in selectivity of carbodiimide insertion are rationalised by in-depth computational studies of the underlying reaction mechanisms.

Results and discussion

Synthesis and characterisation of 1-zirconacyclobuta-2,3-dienes

Challenged by the formation of C–H activation products from complexes **2a** and **2b** that compromise investigations of the reactivity of these unusual species, we have first evaluated the synthesis of more stable derivatives. Use of *ansa*-zirconocene dichlorides [*ansa*-Cp′$_2$ZrCl$_2$] that contain η^5-indenyl instead of η^5-tetrahydroindenyl fragments proved to give the corresponding zirconacycles *rac*-(ebi)Zr(Me$_3$SiC$_3$SiMe$_3$) (**2c**, ebi = 1,2-ethylene-1,1′-bis(η^5-indenyl)) and *rac*-(sbi)Zr(Me$_3$SiC$_3$SiMe$_3$) (**2d**, sbi = dimethylsilylene-1,1′-bis(η^5-indenyl)) in excellent yields of up to 90% (Scheme 1) in the reaction with [Li$_2$(Me$_3$SiC$_3$SiMe$_3$].[22]

^{1}H NMR spectra of both complexes show diagnostic doublet signals at δ 5.84 (**2c**) and 5.97 ppm (**2d**) that correspond to the C–H protons of the cyclopentadienyl fragment adjacent to the bridging unit. In ^{13}C{^{1}H} NMR spectra, the carbon atoms of the metallacycle resonate at 145.2/172.7 (**2c**) and 140.2/180.1 ppm (**2d**), the latter values corresponding to



Scheme 1 Preparation of new 1-zirconacyclobuta-2,3-dienes.

the metal bound C atoms, respectively. Notably, both complexes are stable in solution for several weeks. Also, heating at 80 °C does not lead to significant degradation (Fig. S11 and S12†), making these compounds excellent candidates for the study of onward reactivity.

The molecular structures (Fig. 2 and Fig. S15†) of both complexes show the metal centre in distorted tetrahedral coordination environment as part of the strained 1-metallacyclobuta-2,3-diene moiety. Bond lengths in this fragment support the assignment as a 1-metallacyclobuta-2,3-diene with C–C bonds well in the range of double bonds (*e.g.*, **2c**: C1–C2 1.311(2), C2–C3 1.308(2) Å, $\sum r_{\text{cov, C,C}} = 1.34\,Å^{23}$). Comparison of the sum of angles around C1 and comparison with the values found for η^5-tetrahydroindenyl complexes reveals that the more rigid η^5-indenyl-based ligands show a less bent geometry and less deviation from planarity (dfp, Fig. 2 right). We therefore expect a higher biradicaloid character in **2c** and **2d** (see below, dfp = (360° – (Σ∡(C1) = 8.1 (**2a**); 8.2 (**2b**); 4.6 (**2c**); 7.9° (**2d**)))).[24]

Attempts to prepare a related titanocene complex using the *rac*-(ebi) ligand were of limited success. While selective initial formation of the desired complex **1c** was evident from the presence of two doublets in the ^{1}H NMR spectrum at δ 5.74 and 6.78 ppm, the complex was found to be unstable in benzene solution, producing the coupling product $Me_3SiC_2C(SiMe_3)$=C$(SiMe_3)C_2SiMe_3$ (**4**, δ 0.20, 0.48 ppm, Scheme 1, Fig. S24 and S25†). Formation of this species is proposed to occur *via* coupling of two metallocene η^2-alkyne-carbene fragments – a mesomeric form of a 1-metallacyclobuta-2,3-diene – and subsequent release of the C_6 product. Such reactivity was described before by us for the [Cp*$_2$Ti] analog[20] as well as by Casey and co-workers for a [CpRe(CO)$_2$] system.[25] At this point, we note that during the follow-up investigation of the already published synthesis of Ti complex **1a** (Fig. S23†), the coupling product **4** could also be identified in the filtrate during the work-up of the reaction solution. A similar behaviour was found for the reaction of Cp_2TiCl_2 that does not result in the formation of the desired metallacycle.[20]

With the knowledge of formation of a new set of *ansa*-indenyl 1-metallacyclobuta-2,3-diene complexes (**1c**, **2c**, **2d**), albeit for a short time in the case of **1c**, we have studied the structure–property relationships of this unusual class of compounds and attempted to explain the reactivity/stability differences between **1c** and **2c**. To this end, we have calculated essential properties at a unified level of theory for the compounds listed in Table 1, which have been isolated or studied experimentally to date. As already described, only in the case of Cp*$_2$Ti the triplet state corresponds to the lowest energy state,[20] which is due to the planar $Me_3SiC_3SiMe_3$ unit. This deviation from planarity (dfp, Fig. 2 right, characterised by the angles around C1 and C3) significantly determines the electronic properties of these systems. Looking at the values summarised in Table 1, it becomes evident that with lower dfp both the singlet–triplet gap $\Delta E_{\text{S–T}}$ and the natural charge $q_{\text{nat.NBO}}$ on the $Me_3SiC_3SiMe_3$ unit decrease. In contrast, the biradicaloid character β[26] of these compounds increases. It is worth noting that when the complexes are grouped into titanocenes and zirconocenes, moderate correlations of the previously discussed values are apparent and the Cp*$_2$Ti complex cannot be included in this correlation of dfp and the $q_{\text{nat.NBO}}$ (Fig. S170–S172†).

The introduction of the η^5-indenyl-based ligands leads to a decrease in the dfp compared to the η^5-tetrahydroindenyl complexes due to their rigidity. Particularly with the reaction behaviour of **1c** in mind, in which the coupling product **4** was identified as a secondary product, it is evident that the biradicaloid character must not be too high in order to allow for isolation of the 1-metallacyclobuta-2,3-diene species. The slightly increased biradical character in **2c** and **2d** combined with the potentially suppressed C–H activation at the metallocene scaffold led us to hope for a more selective and possibly different reactivity of these representatives compared to **2a** and **2b**.

Reactivity with carbodiimides

Formation of four-membered 2-aza-1-metallacyclobut-3-ene complexes. To evaluate the reactivity of the four-membered metallacycles, we have performed reactions of complexes **2a–d**, as well as the Ti analog **1a**[27] with five different carbodiimides RN═C═NR (R = iPr, Cy, *p*-Tol, SiMe$_3$, Dipp; *p*-Tol = 4-methylphenyl, Dipp = 2,6-diisopropylphenyl). To our surprise,

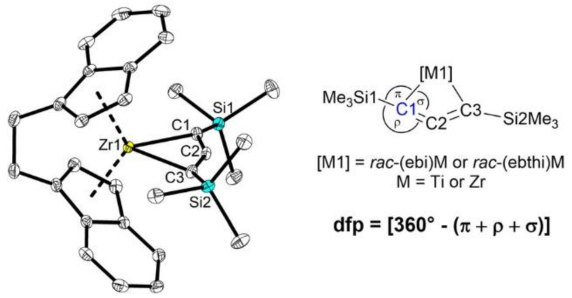
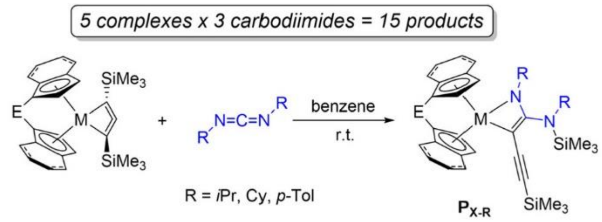


Fig. 2 Left: molecular structure of complex **2c**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity; Right: scheme for calculation of dfp values.

Table 1 Comparison of calculated features of 1-metallacyclobuta-2,3-dienes, calculated at the B3LYP/GD3BJ/def2tzvp level of theory

Metallocene	$\Delta E_{\text{S–T}}$ [kJ mol^{-1}]	dfp (C1) [°]	$q_{\text{nat.NBO}}$ (allene)	β^a [%]
Cp_2Ti (**A**)	−24.3	2.9	−0.52	29.8
Cp*$_2$Ti (**B**)	9.9	0.2^b/0.0^c	−0.94^b/−0.58^c	75.8
rac-(ebthi)Ti (**1a**)	−41.4	7.4	−0.74	24.0
rac-(ebi)Ti (**1c**)	−25.2	4.7	−0.62	34.5
rac-(ebthi)Zr (**2a**)	−99.8	9.4	−0.98	1.9
rac-(sbthi)Zr (**2b**)	−96.9	7.2	−0.95	2.7
rac-(ebi)Zr (**2c**)	−81.6	5.5	−0.91	3.3
rac-(sbi)Zr (**2d**)	−78.7	4.9	−0.88	4.9

[a] See ESI,† section 9.3.6 for further details. [b] Values for the optimised geometry of the singlet state. [c] Values for the optimised geometry of the triplet state.



	tetrahydroindenyl complexes			*indenyl complexes*	
	1a	2a	2b	2c	2d
R = *i*Pr	$\mathrm{P}_{1a\text{-}i\mathrm{Pr}}$	$\mathrm{P}_{2a\text{-}i\mathrm{Pr}}$	$\mathrm{P}_{2b\text{-}i\mathrm{Pr}}$	$\mathrm{P}_{2c\text{-}i\mathrm{Pr}}$	$\mathrm{P}_{2d\text{-}i\mathrm{Pr}}$
R = Cy	$\mathrm{P}_{1a\text{-}\mathrm{Cy}}$	$\mathrm{P}_{2a\text{-}\mathrm{Cy}}$	$\mathrm{P}_{2b\text{-}\mathrm{Cy}}$	$\mathrm{P}_{2c\text{-}\mathrm{Cy}}$	$\mathrm{P}_{2d\text{-}\mathrm{Cy}}$
R = *p*-Tol	$\mathrm{P}_{1a\text{-}p\text{-}\mathrm{Tol}}$	$\mathrm{P}_{2a\text{-}p\text{-}\mathrm{Tol}}$	$\mathrm{P}_{2b\text{-}p\text{-}\mathrm{Tol}}$	$\mathrm{P}_{2c\text{-}p\text{-}\mathrm{Tol}}$	$\mathrm{P}_{2d\text{-}p\text{-}\mathrm{Tol}}$

Scheme 2 Formation of 2-aza-1-metallacyclobut-3-ene complexes.

DippN═C═NDipp did not show reactivity with any of the group 4 metal complexes at room temperature or 80 °C, which contrasts with the reactivity of metallocene alkyne complexes, where this carbodiimide as well as the Mes analog (Mes = 2,4,6-Me-C_6H_2) underwent cleavage of the N–C bonds in reactions with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[13b] This clearly highlights the electronical difference in the starting complexes. In reactions of RN═C═NR (R = iPr, Cy, *p*-Tol) with all complexes studied, formation of four-membered 2-aza-1-metallacyclobut-3-ene complexes $\mathbf{P}_{\mathbf{X\text{-}R}}$ occurs selectively (Scheme 2). All complexes were fully characterised, including X-ray analysis for six derivatives (see ESI† for details). All complexes show $^{13}C\{^1H\}$ NMR values for the internal carbon atom of the activated carbodiimide at 140–152 ppm, which is slightly deshielded compared to the free substrate (R = iPr: 140.2, R = Cy: 139.7, R = *p*-Tol: 136.4 ppm), depending on the substituent used. Whereas zirconium bound C atoms resonate at 144–152 ppm, the values for the lighter Ti congeners are found at much lower field (168–183 ppm).

The molecular structures of six of these complexes were determined by SC-XRD measurement from which $\mathbf{P}_{\mathbf{2a\text{-}iPr}}$ (Fig. 3) is discussed as an example. It shows the bent metallocene coordinated with the amido ligand. The C–C (1.398(2) Å) and C–N bond lengths (1.402(2) Å) confirm this species as a 2-aza-1-metallacyclobut-3-ene $\left(\sum r_{\text{cov},\,\text{C,C}} = 1.34\,\text{Å}\right)$.[23] The main differences in these complexes are the usual shorter M–N and M–C bonds in the titanacycles consistent with larger N–Ti–C angles and smaller N–C–C angles compared to the zirconium complexes (Table S3†). Such species are well-studied intermediates in [2 + 2] cycloaddition reactions of metal imido complexes and alkynes.[28] The formation of the herein described complexes occurs *via* formal 1,2-insertion of the carbodiimide, haptotropic change of the allenediide ligand and migration of a $SiMe_3$. The shift of a $SiMe_3$ group along multiple bonds is well-precedented for organometallic[29] and main group-based systems[30] containing unsaturated structural motifs. A similar observation was made in reactions of related group 4 metallocene alkyne complexes with carbodiimides. In these cases activation of metal-coordinated bis(trimethylsilyl)acetylene occurred to produce 2-aza-1-metallacyclopenta-3,4-enes (Fig. 1a).[12,13]

Formation of six-membered metallacycloallene complexes. Reactions of η^5-tetrahydroindenyl complexes **1a**, **2a**, and **2b** with $Me_3SiN{=}C{=}NSiMe_3$ did not produce similar metallacyclic structures. Whereas the Ti complex **1a** showed no conversion at elevated temperatures, the Zr complexes **2a** and **2b** were transformed into the C–H activation products **3a**/**3b** that were described before.[21] In contrast, η^5-indenyl complexes **2c** and **2d** could be converted within minutes at room temperature, producing a single new metallocene species that, according to its ^1H and $^{13}C\{^1H\}$ NMR spectra is not consistent with the four-membered aza-metallacyclobutene structure (Scheme 3). Instead, well-separated $^{13}C\{^1H\}$ resonances at 159.6/174.4 ($\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$) and 157.9/176.0 ppm ($\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$) as well as prominent IR bands at 1852 ($\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$) and 1849 cm^{-1} ($\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$) suggest the presence of an intact allene unit. This is corroborated by the molecular structure of these complexes that shows the metal centre as part of a 2-aza-1-metallacyclohexa-2,4,5-triene unit (Fig. 4). Of note, analytically pure complexes $\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$ and $\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$ slowly decompose into the corresponding 1-zirconacyclobuta-2,3-diene and $Me_3SiN{=}C{=}NSiMe_3$ at room temperature, while a slight excess of $Me_3SiN{=}C{=}NSiMe_3$ can suppress this process.

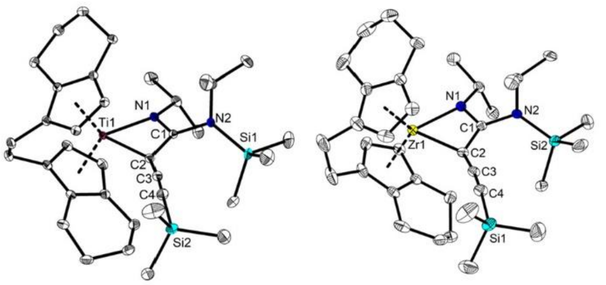
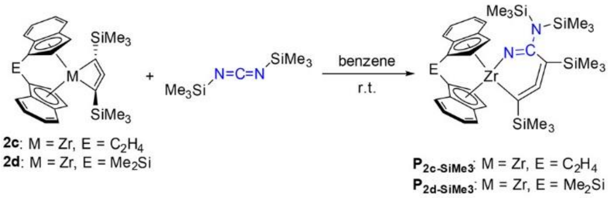


Fig. 3 Molecular structure of complexes $\mathrm{P}_{1a\text{-}i\mathrm{Pr}}$ (left) and $\mathrm{P}_{2a\text{-}i\mathrm{Pr}}$ (right). Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.



Scheme 3 1,2-Insertion of $Me_3SiN{=}C{=}NSiMe_3$ into η^5-indenyl substituted 1-zirconacyclobuta-2,3-dienes.

Bond lengths in the allene unit are in agreement with slightly shortened and elongated C–C double bonds (*e.g.*,

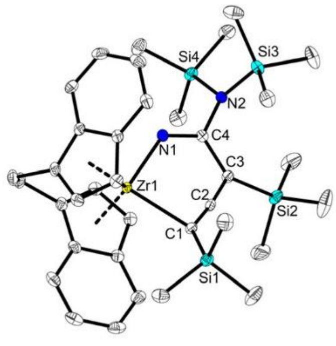


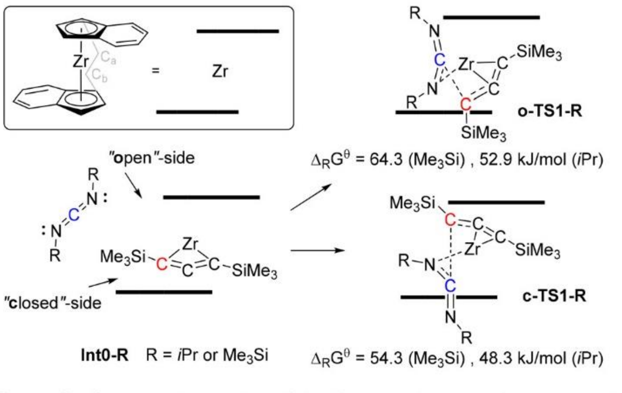
Fig. 4 Molecular structure of complex $\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

$\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$: C1–C2 1.259(3), C2–C3 1.383(3) Å) and significantly different from the starting material **2c** (*vide supra*). The C4–N1 bond (1.309(3) Å) corresponds to an elongated double bond $\left(\sum r_{\mathrm{cov,C,N}} = 1.27\,\text{Å}\right)$.[23] A closer inspection of the geometry of these six-membered 2-aza-1-metallacyclohexa-2,4,5-trienes reveals an envelope type folding that is best defined by two planes (Zr1–C1–C2–C3 and Zr1–N1–C4–C3) with angles between these planes of 33° in $\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$ and 37° in $\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$ (Fig. S20 and S21†).[31] Due to this folding two conformers are possible in these structures, showing either (i) orientation of the Me_3Si groups of the former carbodiimide towards the indenyl unit or (ii) orientation of these groups towards the "open" side of the *ansa*-metallocene, *i.e.*, away from the indenyl group. To our surprise only the first arrangement was observed in metallacycles $\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$ and $\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$. It should be noted that due to the racemic nature of the *C*2 symmetric *ansa*-ligands two isomers are observed in all herein described cases.

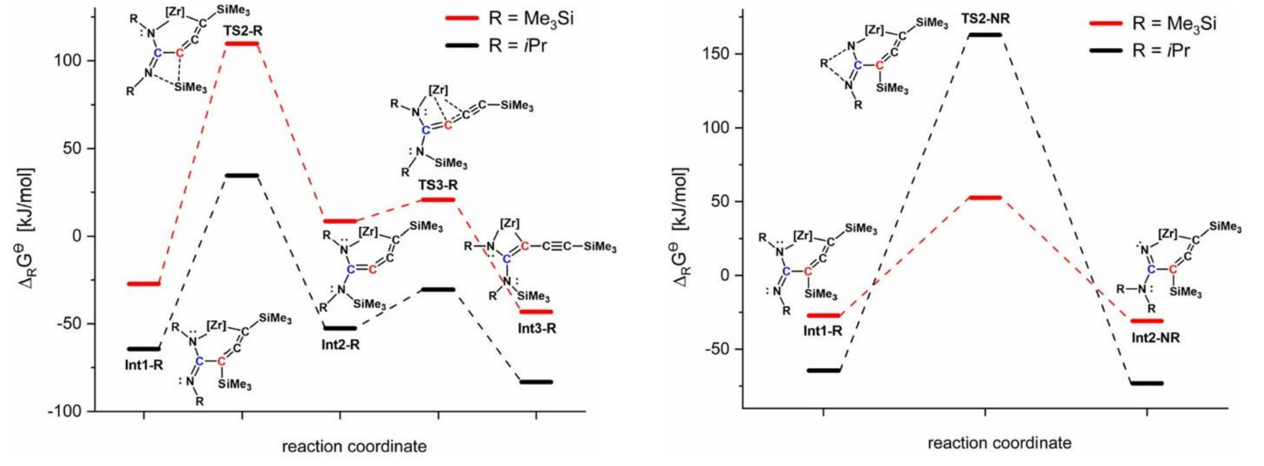
Computational studies of carbodiimide insertion. While the formation of all species formed with carbodiimides described herein involves elements of formal 1,2-insertion of the substrate into the Zr–C bond of the 1-metallacyclobuta-2,3-diene and migration of a $SiMe_3$ group, followed by haptotropic shift of the allene unit, the exact nature of this process is unclear. Of note, the observed reactivities are identical for a large set of *ansa*-Cp′ ligands and carbodiimides (Scheme 2). However, the deviating reactivity of the Dipp and $SiMe_3$ substituted carbodiimides leaves open questions. We have therefore performed a DFT study using selected coupling products as model complexes, focusing on the following questions: (i) Why does the Dipp carbodiimide not react with any of the 1-metallacyclobuta-2,3-dienes? (ii) Why is a completely different reactivity found for the Me_3Si substituted carbodiimide leading to 2-aza-1-metallacyclohexa-2,4,5-trienes? (iii) Why is only one conformer formed for this product class? (iv) Why is this reactivity restricted to the η^5-indenyl substituted zirconocenes?

To shed light on the first two questions, it is obvious to first evaluate simple thermodynamics for the formation of selected examples (Table S4†). We have therefore first performed structure optimisations and confirmed the structures to be local minima on the potential energy surface by harmonic vibration frequency calculation on the same level of theory (B3LYP[32]/GD3BJ[33]/def2tzvp[34]). All reaction enthalpies analysed in this context show exothermic values ranging from −17.9 kJ mol^{-1} ($\mathbf{P}_{\mathbf{1a\text{-}Dipp}}$) to −159.9 kJ mol^{-1} ($\mathbf{P}_{\mathbf{2d\text{-}iPr}}$). However, a comparison of the Gibbs free energy values clearly reveals that the formation of the Dipp substituted 2-aza-1-metallacyclobut-3-ene complexes is strongly endergonic ($\Delta_R G^\theta$ = 77.2 ($\mathbf{P}_{\mathbf{1a\text{-}Dipp}}$); 51.2 kJ mol^{-1} ($\mathbf{P}_{\mathbf{2a\text{-}Dipp}}$)). Supported by an IRI (Interaction Region Indicator[35]) analysis of these two structures, which clearly highlight repulsive interactions of the Dipp, Me_3Si and *rac*-(ebthi) units, the absence of reactivity is nicely explained (Table S5†). In addition, the energetic differences between the elusive Me_3Si substituted 2-aza-1-metallacyclobut-3-ene complexes and the experimentally observed 2-aza-1-metallacyclohexa-2,4,5-triene complexes of the Zr indenyl species are shown to be small. While the formation of both products is exergonic, in the case of [*rac*-(ebi)Zr], the formation of the isolated six-membered product is slightly preferred ($\Delta\Delta_R G^\theta$ = −4.1 kJ mol^{-1} ($\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$)). In contrast, for [*rac*-(sbi)Zr] the four-membered metallacycle is slightly favoured ($\Delta\Delta_R G^\theta$ = 3.4 kJ mol^{-1} ($\mathbf{P}_{\mathbf{2d\text{-}SiMe3}}$)). Since these small energetic differences do not account for the exclusive formation of the experimentally observed species, we analysed the activation barriers along the reaction pathways to the respective complexes, focusing on the reaction pathways leading to $\mathbf{P}_{\mathbf{2c\text{-}iPr}}$ and $\mathbf{P}_{\mathbf{2c\text{-}SiMe3}}$. A total of 80 different geometries and isomers were optimised, the most important results of which will be discussed here.[36] Due to the *C*2-symmetric *ansa*-Cp′ ligand, we considered both an "open" (denoted as "o") and a "closed" (denoted as "c") coordination pathway for entry into the primary coordination sphere of the zirconocene, leading to two different orientations of the first transition state (Scheme 4; **o/c-TS1-R**; R = iPr, Me_3Si). To our surprise, the closed pathway was found to be energetically preferred, presumably due to additional van der Waals interactions between the indenyl and R substituents (Tables S7 and S8†), providing an explanation to answer the third question.

The following C–C bond formation leading to the six-membered 2-aza-1-metallacyclohexa-4,5-diene intermediate struc-



Scheme 4 Computed energies of the first reaction step, *i.e.*, approach of the carbodiimide, in an open (o) and closed (c) orientation. The inset shows the orientation of the bridging C_2H_4 fragment.



Scheme 5 Calculated energetic profiles for the formation of 2-aza-1-metallacyclobut-3-ene complexes (left) and 2-aza-1-metallacyclohexa-2,4,5-triene complexes (right). Energies are referenced to the corresponding **Int0-R**.

tures is in both cases highly exothermic and exergonic (Scheme 5, left and right; **c-TS1-R→Int1-R**). Starting from this intermediate, two pathways are possible: (i) shift of the Me_3Si group from the former 1-zirconacyclobuta-2,3-diene to a nitrogen atom of the previous carbodiimide (Scheme 5 left; **Int1-R→TS2-R**), and (ii) the transfer of the R group between nitrogen atoms of the carbodiimide (Scheme 5, right; **Int1-R→TS2-NR**). While the former step, leading to **TS2-SiMe$_3$** is highly disfavored, the latter transformation to **TS2-NSiMe$_3$** is much lower in energy ($\Delta\Delta_RG^\theta = -57.2$ kJ mol^{-1}), which nicely explains the exclusive formation of the six-membered 2-aza-1-metallacyclohexa-2,4,5-triene complexes for the Me_3Si substituted carbodiimide.

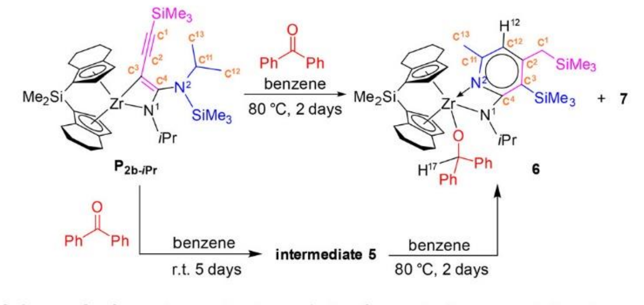
Furthermore, the exclusive formation of the four-membered 2-aza-1-metallacyclobut-3-ene complexes in the case of iPrC=N=CiPr can be rationalised by the inverse energetic situation of these second transition states ($\Delta\Delta_RG^\theta = 128.3$ kJ mol^{-1}). To support the mechanism proposed here, reactions of **2c** with RN=C=NR (R = iPr, $SiMe_3$) were performed at low-temperature and monitored by NMR spectroscopy. For R = iPr formation of an intermediate could already be detected at −50 °C. The ^1H and $^{13}C\{^1H\}$ NMR signatures of this species are consistent with the proposed structure **Int1-iPr**, showing an intact C_3 allene unit (Fig. S9 and S10†). For R = $SiMe_3$, however, no intermediate species could be detected, which is consistent with a slightly higher first activation barrier for the reaction of $Me_3SiN{=}C{=}NSiMe_3$ (Scheme 4, **Int0-R→c-TS1-R**) and the lower second barrier ($\Delta\Delta_RG^\theta$ = (**Int1-SiMe$_3$→TS2-NSiMe$_3$**) = 79.8 kJ mol^{-1} *vs.* (**Int1-iPr→TS2-iPr**) 99.0 kJ mol^{-1}). Complex **P$_{2c\text{-}iPr}$** probably formed *via* the unusual cumulene structure **Int2-iPr** and a low lying **TS3-iPr** (Scheme 5, left). An additional third pathway was considered where the formation of **P$_{2c\text{-}iPr}$** occurs *via* four- membered transition states and intermediates, but this proofed to be disfavoured.

While carefully comparing the structure of **Int2-NSiMe$_3$** with the experimentally determined structure of **P$_{2c\text{-}SiMe3}$**, we noticed a difference in the orientation of the C_2H_4 bridge that was previously overlooked. In **Int2-NSiMe$_3$**, the C_b atom (Scheme 4, inset) points away from the opposing indenyl unit, whereas this is reversed for the product **P$_{2c\text{-}SiMe3}$**. This process of bridge flip is associated with a minor activation barrier *via* a transition state that possesses an almost perpendicular arrangement of the C_2H_4 linkage and the indenyl units (Δ_RG^θ (**Int2-NSiMe$_3$→TS3-NSiMe$_3$**) = 8.6 kJ mol^{-1}). The final intermediate **Int3-NSiMe$_3$** is consistent with the SC-XRD structure and is slightly lower in energy compared to the previous intermediate ($\Delta\Delta_RG^\theta = -2.5$ kJ mol^{-1}). Since it is unclear whether the bridge flip occurs before the reaction with carbodiimide or at the end, as just described, we have also examined it exemplarily for the 1-metallacyclobuta-2,3-dienes **1a, 2a** and **2c**. The bridge flip activation barriers are all low in energy (Δ_RG^θ = 17.9 (**f-1a-TS**); 20.7 (**f-2a-TS**); 22.1 kJ mol^{-1} (**f-2c-TS**)) and the final flipped structures are energetically slightly disfavoured (Δ_RG^θ = 8.9 (**f-1a**); 7.8 (**f-2a**); 11.0 kJ mol^{-1} (**f-2c**), Scheme S8†). Nevertheless, these small values could indicate an equilibrium of both structures in solution at ambient conditions.

To evaluate whether the above-described reaction sequence to form **P$_{2c\text{-}SiMe3}$** is also feasible for these flipped structures and to address the last open question we calculated this sequence for the corresponding zirconocenes (denoted **f-2a** and **f-2c**, Scheme S10 and Table S14†). In both cases, the first transition state energy is the highest along the reaction sequence, but significantly less energy is required for the *rac*-(ebi)Zr compared to *rac*-(ebthi)Zr system (Δ_RG^θ = 49.4 (**f-TS1-2c**); 65.1 kJ mol^{-1} (**f-TS1-2a**)). Following the reaction path, the energies of the η^5-tetrahydroindenyl derivatives are also considerably higher than those of the η^5-indenyl derivatives. In addition, the total energy gain for the formation of **P$_{2c\text{-}SiMe3}$** is higher than the energy barrier for the first transition state which contrasts with **P$_{2a\text{-}SiMe3}$** (Δ_RG^θ = −61.0 (**f-Int2-2c**); −47.2kJ mol^{-1} (**f-Int2-2a**)). Together with the intramolecular competition reaction of C–H bond activation of *rac*-(ebthi) ligand, this offers a plausible explanation for the last question. It can further be speculated that the slightly increased biradical character of **2c** and **2d** (Table 1) has an influence on the reactivity of these species.

Reactivity with carbonyl compounds. As an example, the reactivity and synthetic potential of the new 2-aza-1-metallacyclobut-3-ene complexes was studied in the reaction of $\mathbf{P_{2b\text{-}iPr}}$ with benzophenone. We would like to note at this point that such reactions typically produce rather complex *in situ* ^{1}H and ^{13}C{^{1}H} NMR spectra and a structural assignment of the species formed is generally very challenging based on NMR spectroscopy. Addition of benzophenone to $\mathbf{P_{2b\text{-}iPr}}$ in benzene at room temperature results in the quantitative formation of a new zirconocene species **5** based on its ^{1}H NMR spectrum. We suggest formation of a PhC(H)O alkoxide unit (δ 6.32 ppm, s, Fig. S9†), likely *via* C–H activation at one of the iPr groups. Unfortunately, the exact nature of this species could not be elucidated. Heating of a benzene solution of species **5** at 80 °C results in full conversion to furnish two new zirconocene complexes **6** and **7** (Scheme 6).

A suitable crystal of complex **6** was grown by storing a mixture of complexes **6** and **7** in pentane at −30 °C and the structure of **6** was confirmed and analysed by X-ray crystallography (Fig. 5). Instead of a four membered ZrNCC metallacycle, a new four membered ZrNCN amide unit was formed, possessing a substituted distorted pyridine ring. This pyridine ring is nearly planar with an angle of 14° between the planes C11–N2–C4–C3 and C11–C12–C2–C3, and the bond lengths are in range 1.374(2)–1.445(2) Å, indicating its aromatic nature. The geometry based HOMA (Harmonic Oscillator Model of Aromaticity)[37] value of 0.804 for this unit supports the description as distorted aromatic pyridine unit.[38] Two different Zr–N bond lengths indicate the presence of covalent (Zr1–N1 2.2630(14) Å) and dative (Zr1–N2 2.4296(15) Å) linkages. The latter value is comparable with those of previously reported Zr–pyridine complexes.[39] Interestingly, the coordination of the newly formed alkoxide with the Zr centre has a significant influence on the spatial conformation of the former *rac*-(sbthi) ligand. This can be seen from the top view (Fig. S22†), where coordination of the alkoxide results in a loss of the typical racemic feature and the *ansa* ligand becomes more symmetric, likely due to the presence of two sterically demanding vicinal phenyl groups.



Scheme 6 Stepwise activation of the 2-aza-1-zirconacyclobut-3-ene $\mathbf{P_{2b\text{-}iPr}}$, formation of complex **6**. The structure of intermediate **5** could not be clarified. Spectroscopic details are given in the ESI.†

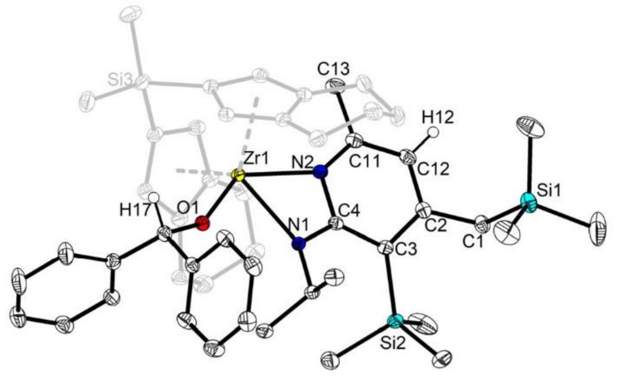


Fig. 5 Molecular structure of complex **6**. Thermal ellipsoids correspond to 30% probability. For clarity, the *ansa*-metallocene fragment is depicted in greyscale and hydrogen atoms (except H12 and H17) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1–N1 2.2630(14), Zr1–N2 2.4296(15), Zr1–O1 2.0130(12), N1–C4 1.349(2), N2–C4 1.381(2), N2–C11 1.374(2), C11–C12 1.383(3), C12–C2 1.401(3), C2–C3 1.404(3), C3–C4 1.445(2), C11–C13 1.505(3), C1–C2 1.508(2), N1–Zr1–N2 56.15(5), N1–C4–N2 108.34(15), C3–C4–N2 121.65(15), C4–N2–C11 119.41(15), C1–C2–C3 122.49(17), C3–C4–N1 130.00(16).

Complex **6** corresponds to a zirconocene(IV) complex that possesses an amidopyridine and an alkoxide ligand. Formation of the former unit can be rationalised by a sequence of multiple bond activation and coupling events, including net twofold C–H activation of an iPr methyl group, C–H cleavage of an iPr methine group, H transfer to the benzophenone substrate and the allene unit, $SiMe_3$ migration from N2 to C3, as well as coupling of the activated iPr group with the allene fragment.

While transition metal-catalysed formation of pyridines by cycloaddition of alkynes and nitriles is a well-established route for the synthesis of functionalised heteroarenes,[40] the herein described route is without precedent. This transformation once again highlights the enormous potential of complexes of electropositive transition metals. It should be interesting to evaluate the reaction principles responsible for this unusual formation of a heteroaromatic compound. Further studies regarding the reaction mechanism and the reactivity of such complexes with related substrates are ongoing in our labs.

Conclusions

Highly unusual group 4 1-metallacyclobuta-2,3-diene complexes offer excellent platforms for studying the insertion reactivity towards unsaturated substrates with carbon-heteroatom bonds. The herein presented reactions of four different carbodiimides RN=C=NR with titanium and zirconium complexes possessing four different *ansa*-cyclopentadienyl ligands result in two different types of structures, namely four-membered 2-aza-1-metallacyclobut-3-enes (R = Cy, iPr, *p*-Tol), where the allene fragment undergoes C–Si activation and isomerisation to an alkynyl group, and six-membered 2-aza-1-metallacyclohexa-2,4,5-trienes (R = $SiMe_3$), formed by simple 1,2-insertion of the carbodiimide and $SiMe_3$ shift. Detailed DFT studies of the mechanisms of formation of these species suggest that the key difference responsible for the presence of two distinct complexes lies in the nature of $SiMe_3$ migration event. While generation of 2-aza-1-metallacyclobut-3-enes for R = iPr and related substituents likely proceeds *via* $SiMe_3$ shift between the allene and carbodiimide fragments, this process is unfavorable for R = $SiMe_3$, where $SiMe_3$ migration across the carbodiimide is preferred. The synthetic potential of these species and of metallacycles based on early transition metals in general for synthetic organometallic and organic chemistry is highlighted in the reaction of a 2-aza-1-zirconacyclobut-3-ene with benzophenone which results in the stepwise formation of a Zr amide complex possessing a substituted pyridyl unit. This species is likely formed *via* an unprecedented sequence of C–H activation, H transfer, $SiMe_3$ migration, as well as C–C bond formation.

With respect to the formation of 1-metallacyclobuta-2,3-dienes, the use of *ansa*-η^5-indenyl instead of *ansa*-η^5-tetrahydroindenyl ligands prevents previously reported C–H activation at the backbone of the cyclopentadienyl ligand. Thus, reactions of complexes possessing these ligands are more selective and allow for reactivity studies at elevated temperatures. A detailed analysis of the electronic structure of a set of hitherto experimentally and computationally studied 1-metallacyclobuta-2,3-dienes shows the general trend of greater biradical character of the Ti complexes with strong influence of the cyclopentadienyl ligands. Based on the synthesis of highly unstable *rac*-(ebi)Ti($Me_3SiC_3SiMe_3$) and previous attempts to prepare [Cp_2Ti] and [$Cp^*{}_2Ti$] derivatives we identified the formation of the C_6 coupling product $Me_3SiC_2C(SiMe_3) = C(SiMe_3)C_2SiMe_3$ and the deviation of the metallacycle from planarity as experimental and structural markers for the biradical character of the respective system.

Author contributions

X. S., S. L., F. R. and T. B. conceived and conceptualised the project. X. S., S. L. and A. S. performed the experiments and analysed the data. F. R. performed DFT calculations and analysed the data. T. B. supervised the project and acquired funding. X. S., S. L., F. R., and T. B. prepared and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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4.3 A general concept for the electronic and steric modification of 1-metallacyclobuta-2,3-dienes: A case study of group 4 metallocene complexes

Sihan Li, Mirjam Schröder, Adrian Prudlik, Xinzhe Shi, Anke Spannenberg, Jabor Rabeah, Robert Francke, Björn Corzilius, Fabian Reiß and Torsten Beweries.

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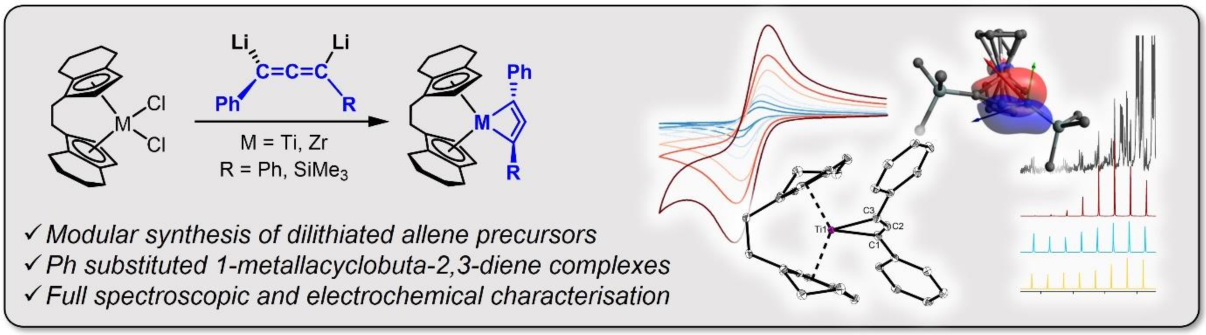

✓ *Modular synthesis of dilithiated allene precursors*
✓ *Ph substituted 1-metallacyclobuta-2,3-diene complexes*
✓ *Full spectroscopic and electrochemical characterisation*

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RESEARCH ARTICLE

A General Concept for the Electronic and Steric Modification of 1-Metallacyclobuta-2,3-dienes: A Case Study of Group 4 Metallocene Complexes

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Dedicated to Prof. Rhett Kempe on the occasion of his 60th birthday

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Abstract: The synthesis of group 4 metal 1-metallacyclobuta-2,3-dienes as organometallic analogues of elusive 1,2-cyclobutadiene has so far been limited to $SiMe_3$ substituted examples. We present the synthesis of two Ph substituted dilithiated ligand precursors for the preparation of four new 1-metallacyclobuta-2,3-dienes [*rac*-(ebthi)M] (M = Ti, Zr; ebthi = 1,2-ethylene-1,10-bis(η^5-tetrahydroindenyl)). The organolithium compounds [$Li_2(RC_3Ph)$] (**1b**: R = Ph, **1c**: R = $SiMe_3$) as well as the metallacycles of the general formula [*rac*-(ebthi)M($R_1C_3R_2$)] (**2b**: M = Ti, $R_1 = R_2$ = Ph, **2c**: M = Ti, R_1 = Ph, R_2 = $SiMe_3$; **3b**: M = Zr, $R_1 = R_2$ = Ph; **3c**: M = Zr, R_1 = Ph, R_2 = $SiMe_3$) were fully characterised. Single crystal X-ray diffraction and quantum chemical bond analysis of the Ti and Zr complexes reveal ligand influence on the biradicaloid character of the titanocene complexes. X-band EPR spectroscopy of structurally similar Ti complexes [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)] (**2a**), **2b**, and **2c** was carried out to evaluate the accessibility of an EPR active triplet state. Cyclic voltammetry shows that introduction of Ph groups renders the complexes easier to reduce. ^{13}C CPMAS NMR analysis provides insights into the cause of the low field shift of the resonances of metal-bonded carbon atoms and provides evidence of the absence of the β-C-Ti interaction.

Introduction

Aspects of structure, bonding, and reactivity of small unsaturated metallacycles are of interest for the inorganic and organometallic community due to the potential of these compounds for small molecule activation and the construction of extended functional π systems.[1] The incorporation of cumulated double bonds further complicates the synthesis of such compounds and usually requires unusual, synthetically challenging ligand precursors.

In the past, highly ring-strained and unsaturated 1-metallacyclobuta-2,3-diene complexes, organometallic analogues of elusive 1,2-cyclobutadienes were discussed as deactivation products in the metathesis of terminal alkynes using group 6 metal complexes[2] (Figure 1a, left).

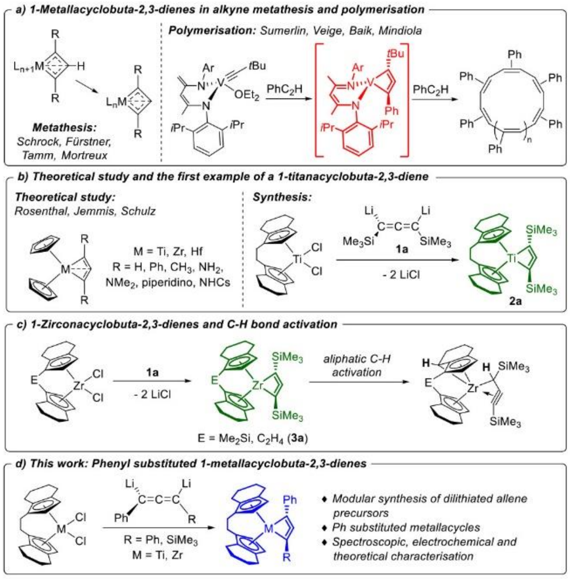


Figure 1. State of the art in view of the chemistry of 1-metallacyclobuta-2,3-dienes (a-c) and outline of the present work (d).

Interestingly, Mindiola and co-workers recently proposed that 1-vanadacyclobuta-2,3-dienes of the general formula [(BDI)V(*t*BuC$_3$Ph)] (BDI = [ArNC(CH$_3$)]$_2$CH, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) are relevant intermediates for the polymerisation of phenyl acetylene with V alkylidyne precatalysts [(dBDI)V(≡C*t*Bu)(OEt$_2$)] (dBDI = ArNC(CH$_3$)CHC(CH$_2$)NAr, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), yielding unusual cyclic alkynes (Figure 1a, right).[3] Formation of this species is suggested to occur by [2+2] cycloaddition of alkyne and alkylidyne, followed by proton shuttling to the dBDI ligand. Isomerisation of the transient 1-metallacyclobuta-2,3-diene could produce a catalytically competent alkynyl-alkylidene species that was described earlier by Mortreux and co-workers.[4]

Synthetic models of such species with potentially redox-inert group 4 metal-ligand scaffolds were not accessible for a long time.[5] As group 4 metallocenes of the type [Cp$_2$M:] are isolobal to carbenes,[6] these organometallic fragments are ideal for the construction and stabilisation of the desired metallacycles. This approach has been utilised on several occasions in the past, e.g., for the synthesis of three- and five-membered saturated and unsaturated metallacycles containing all-carbon as well as heteroatom scaffolds.[7]

In previous work, we have demonstrated that *ansa*-metallocenes are particularly well suited for the preparation of unusual 1-metallacyclobuta-2,3-dienes. Reaction of a dilithiated allene precursor [Li$_2$(Me$_3$SiC$_3$SiMe$_3$)] (**1a**)[8] with [*rac*-(ebthi)TiCl$_2$] resulted in the formation of the first stable 1-titanacyclobuta-2,3-diene [*rac*-(ebthi)Ti(Me$_3$SiC$_3$SiMe$_3$)] (**2a**, Figure 1b, right). Later, this conceptionally simple preparative approach was transferred to the corresponding *ansa*-zirconocene analogue **3a** and a related Me$_2$Si bridged system (Figure 1c).[9] However, in these cases, intramolecular C-H activation at the tetrahydroindenyl unit of the *ansa* ligand, producing stable propargyl complexes, was a side effect that diminished the yields of the desired metallacyclic products. Use of η^5-indenyl containing ligand systems prevents undesired C-H activation reactions and allows for the preparation of thermally stable 1-zirconacyclobuta-2,3-dienes.[10] The reactivity of these species is to date dominated by classical metallacycle-type behaviour with 1,2-insertion of the respective substrate being the first step in all cases. This is followed by cycloreversion of the thus formed metallacycle in reactions with carbonyl compounds,[11,9] or substrate-divergent migration of SiMe$_3$ groups in reactions with carbodiimides.[10]

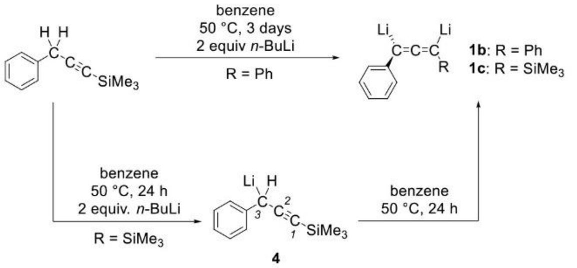
While first studies of the reactivity of these isostructural Ti and Zr complexes revealed a similar behaviour, theoretical analysis of these systems suggests the presence of a pronounced biradicaloid electronic structure exclusively for the titanacycles that is strongly dependent on nature of the metallocene scaffold.[11,10] For example, complex **2a** exhibits unique biradicaloid character due to the presence of antiferromagnetically coupled Ti(III)/alleneylide ligand system (Figure 1a).[11] While we found an even greater biradical character for non-bridged Cp (Cp = η^5-cyclopentadienyl) and Cp* (Cp* = η^5-pentamethylcyclopentadienyl) based systems, the presence of the *ansa*-ligand turned out to be the key for the stabilisation of such unusual species at room temperature. An experimental investigation of this binding situation, including EPR spectroscopic analysis of the singlet-triplet transition, has not been carried out to date. In a previous communication it was shown that the electronic nature of these highly unusual four-membered metallacycles depends strongly on the α-substituents, adjacent to the metal centre, and that these systems can be stabilised by a transannular β-C-Ti binding interaction (Figure 1b, left).[12] Such modifications should allow to tune this unit sterically and electronically, with consequences for the reactivity of the respective 1-metallacyclobuta-2,3-dienes in stoichiometric and catalytic transformations.

However, variation of the α-substitution pattern of 1-metallacyclobuta-2,3-dienes was not reported to date. Herein we present the synthesis and characterisation of suitable phenyl substituted organolithium ligand precursors along with the application of these species to the synthesis of phenyl-substituted group 4 1-metallacyclobuta-2,3-dienes (Figure 1d). Detailed spectroscopic, electrochemical, and theoretical analysis of these complexes gives insights into the unique structure and electronic nature of these species as well as the previously reported analogues.

Results and Discussion

Synthesis and characterisation of phenyl substituted dilithioallene precursors

Since [Li$_2$(Me$_3$SiC$_3$SiMe$_3$)] has been successfully utilised as a dilithiated allene precursor in the preparation of a series of non-metallocene as well as *ansa*-metallocene-based metallacyclobuta-2,3-dienes [LM(Me$_3$SiC$_3$SiMe$_3$)] (M = Ti, Zr, V; L = *ansa*-cyclopentadienyl or BDI with BDI = ArNC(CH$_3$)CHC(CH$_3$)NAr, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[11,9,10,3] we used the same strategy to synthesise the 2,4-diphenyl and unsymmetrically substituted 2-trimethylsilyl-4-phenyl substituted 1-metallacyclobuta-2,3-dienes. As in our previous work, we aimed to avoid the in-situ synthesis of the organolithium compound.[13] Reaction of 1,3-disubstituted propyne precursors with two equivalents of *n*-BuLi in benzene at 50 °C results in the formation of dilithiated allenes [Li$_2$(PhC$_3$Ph)] (**1b**) and [Li$_2$(Me$_3$SiC$_3$Ph)] (**1c**) that can be isolated as pyrophoric red and yellow solids, respectively (Scheme 1).



Scheme 1. Synthesis of dilithiated allene precursor **1b**, **1c**, and **4** as an intermediate for the formation of **1c**.

The ^{1}H NMR spectra of these species exclusively show signals for both compounds in the aromatic and high field region (SiMe$_3$

group of **1c**), indicating that abstraction of the CH_2 protons from the propyne was successful. The ^{13}C NMR spectra of both compounds show characteristic signals for the internal carbon atoms at δ 202.0 (**1b**) and 159.4 ppm (**1c**), respectively. A summary of spectroscopic data of these compounds is given in Table 1. Attempts to crystallise compound **1b** to determine its molecular structure by single-crystal X-ray diffraction analysis (SC-XRD) reproducibly led to decomposition and formation of an unusual compound that contains the desired structural motif of a dilithiated allene, albeit with an additional oxygen atom, likely derived from the presence of a sub-stoichiometric amount of water, that is coordinated by six Li atoms, as well as two molecules of an unusual cyclobutyl fragment, formed by coupling of the allene (Figure S35).[13b,14]

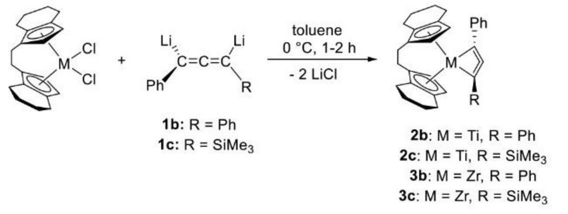
For compound **1c**, ^1H NMR analysis of the reaction mixture showed that deprotonation occurs in stages (Scheme 1): A singlet resonance at δ 3.37 ppm that corresponds to a methine proton clearly indicates the presence of singly deprotonated intermediate **4** after a reaction time of only one day (Figure S18). The molecular structure of **4** was confirmed by SC-XRD (Figure S36) and shows three molecules of THF coordinated to the alkyne-bound Li atom (labelling see Scheme 1: C1-C2 1.221(3), C2-C3 1.399(3) Å; for further information, see the SI).

Colourless crystals of **1c** suitable for SC-XRD analysis were obtained at -78 °C from THF/hexane solution. The molecular structure of **1c** is shown in Figure S37 and confirms the presence of the desired asymmetric dilithioallene structure, comprising of a cluster containing 13 Li atoms and five units of the dilithiated allenediide. In addition, in one of the units a Ph group is deprotonated in *ortho* position. Furthermore, two *n*-butyl groups and three THF molecules stabilise the cluster, leading to the overall formula $[Li_{13}(Me_3SiC_3Ph)_4(Me_3SiC_3C_6H_4)(C_4H_9)_2(C_4H_8O)_3\cdot C_6H_6]$.

Formation of clusters is well-established in organolithium chemistry, illustrating the challenging synthesis conditions associated with the high reactivity.[15] Taken together, the SC-XRD analyses of **1b**, **1c**, and **4** indicate the successful synthesis of the dilithiated metallacyclobutadiene precursors, confirming that deprotonation of substituted propynes provides a general entry to this synthetically useful class of organolithium compounds. However, potential difficulties in handling the phenyl-substituted derivatives are already indicated, which could lead to undesired side reactions and reduced yields due to ortho-metallation and *n*-BuLi inclusion.

Synthesis and characterisation of 1-metallacyclobuta-2,3-diene complexes

To evaluate the thermodynamic feasibility of the formation of phenyl-substituted metallacycles possessing *rac*-(ebthi) ligands, we have first analysed isodesmic exchange reactions on the B3LYP[16,17]-D3[18]/def2-TZVP[19,20] level of theory (Scheme S1, Table S14). The calculated Gibbs free energies are located the range $-15.8 < \Delta_R G° < -11.8$ kcal·mol^{-1}, indicating that formation of Ti- and Zr-based metallacycles is exergonic. Indeed, reaction of the dilithiated phenyl substituted allene **1b** with [*rac*-(ebthi)MCl_2] (M = Ti, Zr) at 0 °C in toluene furnishes new 1-metallacyclobuta-2,3-diene complexes **2b** and **3b** (Scheme 2).



Scheme 2. Synthesis of Ph substituted 1-metallacyclobuta-2,3-diene complexes.

Both compounds show the expected characteristic ^1H NMR signals (**2b**: δ 6.68, 5.64; **3b**: δ 6.36, 5.66 ppm) corresponding to the Cp protons of the *rac*-(ebthi) ligand. In ^{13}C NMR spectra, the signals of the metal bound C atoms of the metallacycle are observed at δ 211.9 (**2b**) and 186.5 ppm (**3b**), which is in the same range as for related complexes reported earlier by our group.[11,9,10] Similarly, reaction of [*rac*-(ebthi)MCl_2] (M = Ti, Zr) with unsymmetrically substituted **1c** at 0 °C in toluene produces complexes **2c** and **3c** (Scheme 2). The ^1H NMR spectra show four informative doublet resonances that can be assigned to the Cp protons due to the non-symmetric structure of the complexes (**2c**: δ 6.98, 6.78, 5.54, 5.41; **3c**: d 6.83, 6.61, 5.59, 5.47 ppm). The ^{13}C NMR spectra exhibit two signals of the metal bound C atoms of the formal allene unit at δ 216.1, 207.1 ppm (**2c**) and 177.7, 176.8 ppm (**3c**). A summary of spectroscopic data for all complexes is presented in Table 1.

The solid-state structures of diphenyl substituted complexes **2b** and **3b** were confirmed by SC-XRD analysis and depicted in Figure 2. Selected bond lengths and angles are listed in Table 1 (for further details, see the Supporting Information). The C-C bond distances of the bent allene sub-unit are in the range of double bonds (see Table1, Σr_{cov}(C=C = 1.34 Å).[21] Both structures are characterised by the well-established M-C_3 four-membered ring with C-C-C angles of 145.27(16)/146.0(2) (**2b**) and 144.6(7)/147.5(7)° (**3b**), respectively: These values are slightly smaller compared to the $SiMe_3$ substituted group 4 1-metallacyclobuta-2,3-dienes (150.08(15)/149.32(12)°, **2a**/**3a**, Figure 1), indicating a small influence on the geometry of the M-C_3 unit by the introduction of the phenyl unit. In line, the M-C1/C3 bond lengths are quite similar; only in **2b** we observed a significant shortening compared to complex **2a** (Table 1).

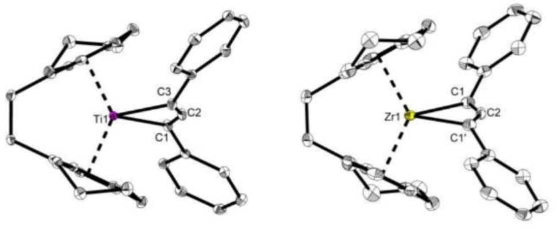


Figure 2. Molecular structures of complexes **2b** (left) and **3b** (right), only one molecule of the asymmetric unit is shown. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

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Table 1. Summary of NMR spectroscopic and structural data of compounds **1b**, **1c**, **2b**, **2c**, **3b**, and **3c**.

	δ(^{13}C) C=*C*=C [ppm]	δ(^{13}C) *C*=C=*C* [ppm]	d(M-C1) [Å]	d(M-C3) [Å]	d(C1-C2) [Å]	d(C2-C3) [Å]	C1-C2-C3 [°]	C1-M1-C3 [°]	dfp(α-C)[a] [°]
1b	202.0	117.2							
1c	159.4	120.0/113.1							
2b	119.3	211.9	2.2016(15) [2.2085(15)] [b] *2.184*[c]	2.2076(15) [2.2085(15)] *2.184*	1.312(2) [1.3127(17)] *1.308*	1.314(2) [1.3127(17)] *1.308*	145.27(16) [146.0(2)] *144.33*	69.28(6) [69.28(8)] *69.52*	14.0/15.5 [13.1] *10.0*
2c	145.4	216.1/207.1	n.a.[d] *2.167(Ph)*	n.a. *2.242($SiMe_3$)*	n.a. *1.317(Ph)*	n.a. *1.289($SiMe_3$)*	n.a. *147.13*	n.a. *69.06*	n.a. *10.9(Ph)/6.8($SiMe_3$)*
3b	139.8	186.5	2.295(5) [2.313(5)] [b] *2.296*	2.295(5) [2.313(5)] *2.296*	1.328(6) [1.316(5)] *1.314*	1.328(6) [1.316(5)] *1.314*	144.6(7) [147.5(7)] *145.20*	66.9(3) [66.2(3)] *66.20*	17.9 [16.0] *13.9*
3c	145.7	177.7/176.8	n.a. *2.291(Ph)*	n.a. *2.326($SiMe_3$)*	n.a. *1.321(Ph)*	n.a. *1.296($SiMe_3$)*	n.a. *147.45*	n.a. *65.93*	n.a. *15.3(Ph)/7.4($SiMe_3$)*
2a[11]	134.2	213.8	2.2287(14) *2.212*	2.2349(15) *2.212*	1.303(2) *1.301*	1.308(2) *1.301*	150.08(15) *149.61*	68.83(6) *69.14*	7.3/6.3 *7.4*
3a[9]	151.4	164.7	2.3099(12) *2.317*	2.3074(12) *2.317*	1.3100(18) *1.305*	1.3076(18) *1.305*	149.32(12) *149.85*	66.28(4) *65.92*	8.1/8.6 *9.4*

[a] dfp(C1): deviation from planarity of C1 atom (dfp = 360 – sum of three angles with C1 as vertices). [b] Numbers given in brackets as the asymmetric unit of **2b** contains one and a half complex molecules, the asymmetric unit of **3b** contains two halves of one complex molecule. [c] Numbers given in italics correspond to calculated values from optimised structures based on the BP86/GD2BJ/def3tzvp level of theory. [d] Not available as these compounds could not be analysed by SC-XRD.

Theoretical analysis of structure and bonding

To better understand the bonding situation of complexes **2b**, **2c**, **3b** and **3c**, especially considering the introduction of phenyl substituents, electron localization function (ELF[22]) analysis were performed (Figure S75-82) in combination with quantum theory of atoms in molecules (QT-AIM[23,24]) analysis shown on the contour plots of the Laplacian operator of electron density alongside the Wiberg binding index (WBI) (Figure 3, Figure S71-S74).
Geometry optimisation on the B3LYP[16,17]-D3[18]/def2-TZVP[19] level of theory gave good agreement of computed and experimental structural parameters for complexes **2b** and **3b** (Table 1). The QT-AIM bond paths of **2b**, **2c**, **3b**, and **3c** are in line with complexes **2a** and **3a**, with two metal-carbon bonds (M-C1 and M-C3) and no significant interaction between the β-carbon atom and the metal centre. Consistent with slightly shorter C2-C3($SiMe_3$) distances compared to the (Ph)C1-C2 distances (Table 1) in the unsymmetrically substituted derivatives **2c** and **3c**, slightly higher WBIs were obtained for bonds to C($SiMe_3$) (C1-C2: 1.77 (**2c**), 1.81 (**3c**); C2-C3: 2.00 (**2c**), 2.00 (**3c**)). These values clearly indicate double bond character in these systems, but also suggest partial polarisation of the allene sub-unit. The ELF plots (Figure S75-S82) of all four new complexes show the absence of localisation of electron density along the M-C2 axis, again illustrating the lack of interaction between β-carbon atom and the metal centre. Furthermore, at this level of theory the formal allendiide character of the C_3 ligand is evident from both the ELF diagrams and the Laplacian plots of the electron density (e.g., Figure 3).
As detailed above, the electronic structure of complex **2a** can be described as a biradicaloid system with antiferromagnetic coupling between a Ti(III) centre and a monoanionic alleneylide ligand, resulting in pronounced biradical character of $\beta_{(8,9)}$[25,26] = 24%, while for the Zr complex **3a** the biradical character can be neglected. Complete Active Space (CAS[2,2]/def2-SVPP) SCF[27] calculations for all new complexes (Figure S61-S62) show $\beta_{(2,2)}$ values of 47% and 56% for complexes **2b** and **2c**, respectively, indicating substantial biradical character for these systems. For complexes **3b** and **3c** much lower $\beta_{(2,2)}$ values of 5% and 4% are observed. A more detailed CAS[8,9]/def2-TZVP calculation (Figure S65-S66) for complexes **2b** and **2c** shows that in both cases, the largest contributions to the multi-determinant wave function are the two determinants placing two electrons either in the formal HOMO (ϕ_4) or LUMO (ϕ_5), giving $\beta_{(8,9)}$ values of 20% (**2b**) and 23% (**2c**), slightly lower than for the $SiMe_3$ complex **2a** (24%). This reveals a clear trend showing that with increasing Ph substitution, the biradicaloid character of the system decreases, which is in line with an increase in the dfp values (Table 1), describing the structural deviation from planarity around the α-C atoms in the metallacycle.[10]

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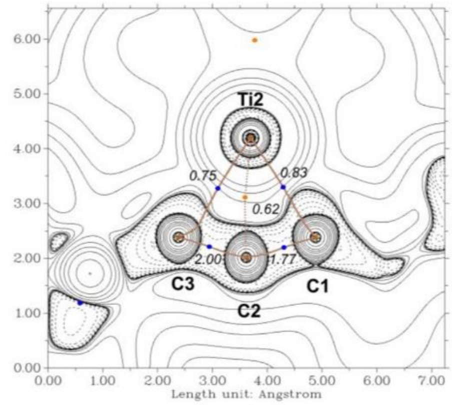

Figure 3. Contour plot of the Laplacian of the electron density $\nabla^2 r$ of complex **2c** in the Ti-(Me_3SiC3-C2-C1Ph) ring plane. Dashed lines indicate negative (local charge concentration), solid lines indicate positive values (local charge depletion). The Laplacian pot is overlaid with the molecular graph from QT-AIM analysis and Wiberg bond indices (italic small numbers). Brown lines indicate bond paths, brown dashed lines are hypothetical bonds, blue dots represent bond critical points; orange dots represent ring critical points.

EPR analysis and quantitative NMR study of paramagnetic species present in Ti complexes

Besides this open-shell singlet biradicaloid state, low lying open-shell triplet states can be assumed. Therefore, we used a DFT approach for computing the singlet-triplet gaps for the Ti complexes ($\Delta E_{S\text{-}T}$ =-9.9 (**2a**), -11.3 (**2b**), -9.4 kcal mol^{-1} (**2c**)). A simple Boltzmann calculation of this singlet-triplet distribution suggests that the triplet state only shows populations of the order of 10^{-9}-10^{-8} and is thus presumably beyond direct experimental observability. To our surprise, EPR spectroscopy yielded clear signals for solutions of all three titanocene complexes **2a-2c** (Figure S48). However, the intensity as well as spectral shape and position of these signals depended on the synthesis batch and the sample shelf time. Therefore, we analysed a sample of **2a** in detail to elucidate the nature of these paramagnetic species. In comparison to literature known complexes,[28] we attribute the detected signals to various Ti(III) impurities that are chemically similar to the monochloride complex [*rac*-(ebthi)TiCl]$_2$ (**5**). We have confirmed that low concentrated solutions of this species **5** show a very similar EPR signature. A more detailed discussion including EPR spectra is presented in the SI (section 5). In short, we concluded that (i) the open-shell singlet state of 1-titanacyclobuta-2,3-dienes cannot be observed by EPR spectroscopy, (ii) thermally induced transition into an EPR active triplet state is not observable (Figure S47), and (iii) EPR active Ti(III) monochloride **5** is present in samples of the 1-titanacyclobuta-2,3-dienes. In addition, in some of the attempts to purify complex **2a** by recrystallisation at -78 °C, formation of green crystals could be observed (Figure S1).[11] SC-XRD analysis confirmed this material to be the complex **5**.[29] Formation of this complex could occur either due to incorrect stoichiometry between organolithium and metallocene dichloride precursors, or by reduction of the Ti(IV) dichloride into the Ti(III) monochloride species **5** by **1a**.[30] Alternatively, previously reported decomposition of the titanacycle[11,10] could result in the formation of $Me_3SiC_2C(SiMe_3)C(SiMe_3)C_2SiMe_3$ and free titanocene [*rac*-(ebthi)Ti]. The latter could undergo redox disproportionation with [*rac*-(ebthi)$TiCl_2$] starting material to produce species **5**.

The identification of a paramagnetic Ti monochloride impurity **5** by EPR spectroscopy as well as SC-XRD analysis prompted us to conduct further Evans NMR analysis using the well-described species **2a** as an example, aiming at the quantification of paramagnetic impurity **5**. Independent synthesis of this species **5** following the literature[31] allowed for quantitative determination of the content of **5** in samples of complex **2a** using the Evans method[32] through a standard addition procedure. Using the residual protio C-H signal of a C_6D_6 filled capillary as a reference (placed into a J. Young tube containing a solution of **2a**/**5** in C_6D_6), a gradual shift to lower field of both, the solvent signal and the resonance of the ebthi ligand of **2a**, can be observed with increasing concentration of **5** (c(**5**): 0-0.0367 mmol/mL, $\Delta\delta$: 22.47-76.39 Hz, Figure S2). Based on these data, a contamination of 13 mol% complex **5** in samples of complex **2a** can be deduced (Figure S4).[33] This method represents a convenient and readily-accessible tool for the identification and quantification of Ti(III) impurities that we recommend to use routinely when synthesizing group 4 metallacycles.

Solid-state NMR analysis

Solid-state NMR (ssNMR) spectroscopy, more specifically the analysis of the three principal components δ_{11}, δ_{22}, and δ_{33} of the chemical shift tensor δ_{iso}, can provide detailed information about the electronic structure (i.e., frontier molecular orbitals) at the observed nuclei of interest, in this case the carbon atoms of the metallacyclic M-C_3 unit.[34] This approach can be applied for the characterisation of ligand properties[35] and organometallic structures such as the unusual cyclic titana-carbene complex [$Cp_2Ti(\kappa^2$-*t*BuNCN*t*Bu)].[36] Furthermore, it can be utilised for the correlation between electronic structure and organometallic and catalytic reactivity.[37]

While ^{13}C CPMAS NMR was performed on compounds **2a** (Table 2) and **2b**, only the former compound produced reasonable spectra. Therefore, the latter is not considered in further analysis (Figure S59-S60). The signal from the carbon atoms C1 and C3 at δ 213.8 ppm in the solution NMR spectrum splits up into two signals at δ 214.1 and 210.9 ppm in the solid state (Figure 4, left). We do not explain this with an electronic difference at the two α-C atoms, but rather assign this to positional disorder (61 %) of one tetrahydroindenyl unit, determined in the SC-XRD analysis, such that complex **2a**[11] is predominantly present in C1 symmetry in the solid state. C1 and C3 atoms show a large deshielding contribution in the δ_{11} value which is in accordance with the natural chemical shielding (NCS) analysis,[34,38] at a truncated model compound [$H_4C_2(C_5H_4)_2Ti(Me_3SiC_3SiMe_3)$]. Due to the highly delocalised and unusual electronic situation, the natural bonding orbital (NBO) programme does not fully resolve this uniformly at the metallacycle, but the resulting natural localised bonding orbitals (NLMOs) and the NCS analysis provide a good

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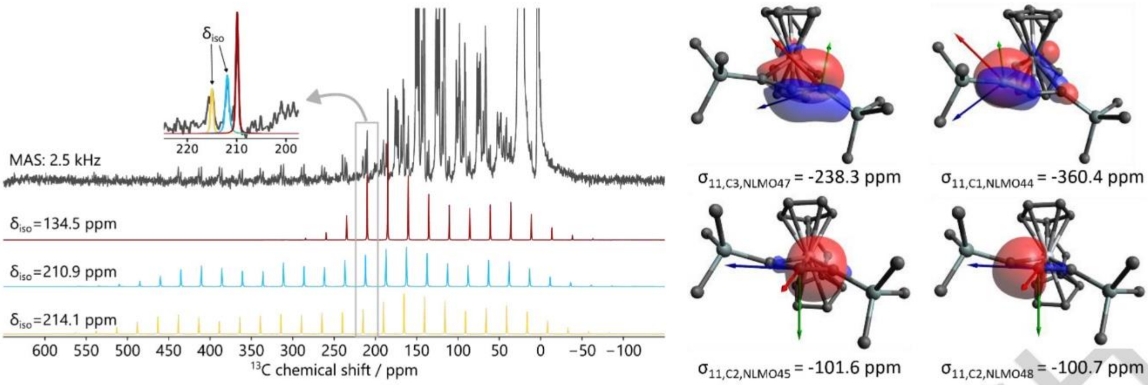

Figure 4. Left: ^{13}C CPMAS NMR spectrum of complex **2a** at a MAS frequency of 2.5 kHz with fitted CSA signals. Right: Illustrations of the NLMOs for the truncated model compound that contribute most to chemical shielding with their absolute shielding values; above for the α-C atoms below for the β-C atom with the principal shielding axes 1 = red, 2= green and 3 = blue; for detailed analysis refer to the Supporting Information Chapter 7.

understanding of the influence of titanium on deshielding. On one carbon, the predominant contributions result from three C1-C2 bond orbitals, one σ and two π bonds. On the other, the deshielding is mainly based on a lone pair at the carbon atom and the Ti-C bond. On both α-C atoms, the NLMOs with the largest contribution to the total deshielding are those that lie in the ring plane and have a significant contribution from a Ti d-orbital (Figure 4, top right: Ti d-orbital contribution NLMO47 = 26% and NLMO44 = 13%). The tensor δ_{11} of the central C_2 atom is significantly lower and does not contain contributions of the Ti orbitals but is mainly based on C2-C σ bonds with the neighbouring carbon atoms (Figure 4, bottom right). It is well-known that metal-bonded carbon atoms, e.g., in metallacycles show significantly more deshielded isotropic chemical shifts than their organic counterparts. Finally, these results provide experimental evidence of the absence of the previously discussed β-C-Ti interaction in these and related systems.[12]

Table 2. Summary of CSA parameters of the relevant carbon atoms of complex **2a**. The values are given in Standard (δ_{11}, δ_{22}, δ_{33}) and Herzfeld-Berger (δ_{iso}, Ω, κ) convention.

Site	δ_{iso} / ppm	δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm	Ω / ppm	κ / ppm
C1/C3	214.1	525.1	149.2	-32.0	557.1	-0.3
C3/C1	210.9	487.7	171.5	-26.5	514.2	-0.2
C2	134.5	242.2	185.7	-24.4	266.6	0.6

Electrochemical analysis of 1-metallacyclobuta-2,3-dienes

Electrochemical analysis of 1-metallacyclobuta-2,3-diene complexes was not performed to date. However, this is particularly interesting for titanium complexes due to the special electronic situation described above with the possible interpretation as a Ti(III) biradical. With the series of structural analogues in hand, we have investigated the influence of the metal and the metallacycle substituents on the electrochemical properties. These studies were conducted to either detect the Ti(III) oxidation state in **2a**, **2b** and **2c**, or alternatively, evaluate the possibility of electrochemically generated Ti(III) intermediates, which could be interesting catalytic intermediates.

The electrochemical behavior of complexes **2b**, **2c**, **3b**, and **3c,** as well as of previously reported complexes **2a** and **3a** was studied using cyclic voltammetry in a solution of 0.1 M Bu_4NBF_4 in THF (see Figure 5 and Table 3). Although 85% of the *iR* drop has been compensated, significant cathodic shifts of the reduction peaks and anodic shifts of the oxidation peaks, respectively, become apparent with increasing scan rate, which can be ascribed to the poor conductivity of the THF-based electrolyte solution. In the reductive regime, each titanocene species (**2a**, **2b**, and **2c**) displays a chemically reversible feature. These features correspond to single electron transfers with equilibrium potentials, E_0(Red), ranging from -1.97 V to -2.06 V vs. Fc/Fc$^+$, whereby the diphenyl substituted complex shows the least negative E_0(red) value. The voltammetric profiles of **2a** recorded at various scan rates are shown exemplarily in Figure 5A. The linear relationship between peak current density (j_p) and the square root of the scan rate (v) indicates a purely diffusive process as predicted by the Randles-Sevcik equation (see Figure 5B).[39] The presence of anodic peaks in the backward scans at low scan rates indicates stability of the singly reduced species even on extended voltammetry timescales. Reductive degradation processes such as demetallation can thereby be excluded. Similar behavior was also observed for species **2b** and **2c** (Figures S50-S51). The chemical reversibility aligns well with the computational results, i.e. that the spin density is located in the Ti d_{z^2}-orbitals of the radical anions (Table S27). Taken together, these findings indicate a metal-centred Ti(IV)/Ti(III) reduction.

As for the reduction, the oxidation potentials of **2a**, **2b** and **2c** are similar to each other, with half-peak potentials, $E_{p/2}$(Ox), between –0.45 V and –0.53 V. However, the corresponding signals display chemical irreversibility, indicating a ligand-centered oxidation that

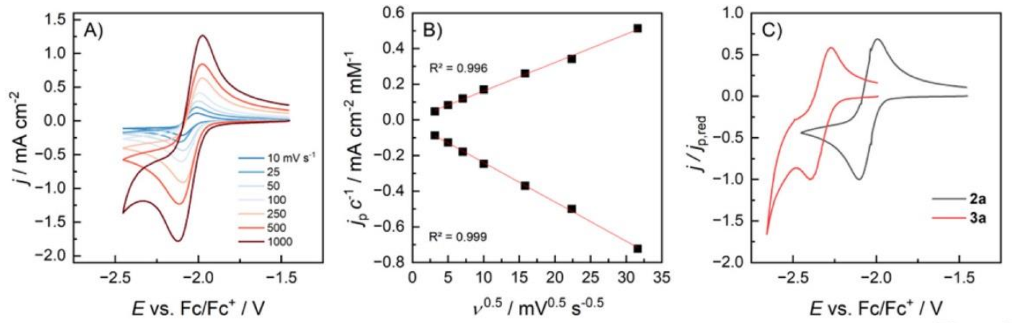

Figure 5. Selected electrochemical data (working electrode: glassy carbon; electrolyte: 0.1 M Bu_4NBF_4 in THF). A): CVs of **2a** recorded at varying scan rates. B) Plot of the peak current densities of Figure 4A versus the square root of scan rate. C) Representative CVs of complexes **2a** and **3a** recorded at v = 100 mV s^{-1} in the negative potential regime.

results in a radical cation which is prone to a chemical follow up reaction. A ligand-centred oxidation would be in line with fully oxidised Ti(IV) complexes and DFT calculations, which indicate the spin localisation at the α-C atoms in the radical cation species (Table S27). Upon expansion of the scan regime to more negative potentials, a second reduction event becomes visible at around -2.5 V with comparably low current densities (Figures S49-S51). This event can be correlated to the Ti(III) monochloride impurity **5** (*vide supra*) by comparison to a separately recorded CV using an authentic sample of **5**. This reduction event is not fully reversible, most probably due to cleavage of the metal-chloride bond.[40] Compound **5** also shows an irreversible oxidation peak at -1.0 V, that can be found in the CVs of **2a**, **2b** and **2c** as well. In good agreement with the Evans quantification method described above, Randles-Sevcik analysis of sample **2a** indicates a content of approx. 9 mol% **5** (assuming single electron transfers and the same diffusion coefficient).

Table 3. Summary of electrochemical data of 1-metallacyclobuta-2,3-diene complexes and the corresponding computed electron affinities (E_A).

	E_0(Red)/V	$E_{p/2}$(Ox)/V	E_A/kJ mol^{-1}
2a	-2.049	-0.447	148.6
2b	-1.967	-0.532	160.1
2c	-2.063	-0.515	156.4
3a	-2.346	[a]	110.3
3b	-2.392	-0.333	121.1
3c	-2.245	-0.584	115.4

[a] For the Zr complex **3a** the oxidation potential is hard to determine due to a very broad peak width.

For Zr complexes **3a**, **3b** and **3c** the electrochemical characteristics are comparable to the Ti analogues, but with negatively shifted E_0(red) values ranging from -2.25 V to -2.39 V. The CV of **3a** recorded at 100 mV s^{-1} is shown exemplarily in Figure 5C. As expected, isostructural Zr complexes show much more negative reduction potentials compared to their Ti counterparts. In contrast, the $E_{p/2}$(ox) values are very similar. The negative shift of the reduction potential correlates well with computed electron affinities (148.6 to 160.1 kJ mol^{-1} for the Ti species and 110.3 to 121.1 kJ mol^{-1} for the Zr analogues, see Table 3).[41] Again, the reductions of all three Zr complexes show reversible characteristics, while the oxidations are irreversible. It should be noted that for **3a** the oxidation potential is hard to determine due to a very broad peak width. Other peaks of possible Zr(III) impurities could not be found. Taken together, the electrochemical data do not provide experimental evidence for the computed partial antiferromagnetically coupled Ti(III)-allenylide biradicaloid character. However, they do reveal potentially electrochemically accessible new radical anionic group 4 1-metallla(III)cyclobuta-2,3-diene complexes that could be relevant for redox-switchable catalytic processes such as alkyne polymerisation.[3]

Conclusion

1-Metallacyclobuta-2,3-dienes are unusual metallacycles that have so far been introduced for a variety of group 4 metallocene frameworks, exclusively based on bis-trimethylsilyl substituted precursors. Their potential relevance in alkyne polymerisation requires the extension of this concept to other substitution patterns. In this work, an approach to the synthesis of further functionalised 1-metallacyclobuta-2,3-dienes is presented for the first time with the introduction of suitable phenyl-substituted organolithium compounds. A ligand influence on the previously observed biradicaloid character of the titanocene complexes could be revealed based on quantum mechanical calculations and crystallographic analysis.

Comparative cyclic voltammetry of a set of structurally related Ti and Zr complexes with different metallacycle substitution patterns shows that the introduction of Ph groups makes the complexes easier to reduce. Detailed EPR spectroscopic analysis of three related Ti complexes provided evidence for the presence of [*rac*-(ebthi)TiCl] as a Ti(III) impurity which is supported by complementary electrochemical and Evans NMR analysis. We showed that the latter method can be readily applied for the rapid detection of paramagnetic impurities in general in organometallic samples. We have additionally used ^{13}C CPMAS NMR spectroscopy as a highly valuable tool for the experimental analysis of the electronic structure of our complexes and of organometallic species in general. Using this technique, we shed light on the cause of the low field shift of the resonances of the metal-bonded carbon atoms and for the first time prove experimentally that there is no through-ring interaction between the metal centre and the central C atom of the metallacycle.

This extension of the chemistry of 1-metallacyclobuta-2,3-dienes and suitable organolithium precursors to prepare these will significantly increase the scope of accessible complexes and allow to tune the steric and electronic profile of these unusual metallacycles, potentially leading to new applications of these complexes in catalysis and small molecule activation.

Experimental Section

Synthesis of complex 1b. A solution of *n*-BuLi (5.06 mmol, 2.0 mL, 2.1 eq, 2.5 mol/L *n*-hexane solution) was added dropwise within 20 min to a pale-yellow solution of 1,3-diphenyl-1-propyne (2.41 mmol, 463 mg, 1.0 eq) in benzene (40 mL) at room temperature. The clear pale-yellow solution was cooled to -78 °C, degassed and heated to 50 °C for 72 h, yielding a gelatinous orange substance. The resulting gel was then washed with *n*-hexane (3 x 10 mL) and dried in vacuo for 8 h to obtain **1b** as a red solid (319 mg, 69%). Single crystals suitable for SC-XRD analysis were grown from THF/*n*-hexane under -78 °C. It should be noted that residual *n*-hexane solvent could not be removed from **1b**, despite repeated washing and prolonged treatment in vacuum. Note: Using a total amount of benzene and hexane of 70 mL as solvents for the reaction. Assuming that these solvents contain traces of water (1 ppm), this leads to a total water content of approximately 0.4 mmol, which cannot be avoided and leads to partial degradation of compound **1b** (see Figure S35). **^{1}H NMR** (25 °C, [D8]THF, 400.13 MHz): δ = 7.15–6.99 (m, 4H), 6.81–6.74 (m, 4H), 6.44–6.32 (m, 2H). **^{13}C NMR** (25 °C, [D8]THF, 100.63 MHz): δ = 202.0 (C=*C*=C), 129.6 (2 x C Ph), 128.7 (4 x *C*H Ph), 127.7 (2 x *C*H Ph), 127.5 (4 x *C*H Ph), 117.2 (2 *C*=C=C). **^{7}Li NMR** (25 °C, [D8]THF, 155.51 MHz): δ = 1.01 (s). **MS-CI$^+$** (isobutane): [(M-2Li)$^+$] 192 (100), [(2M-4Li)$^+$] 384 (94). **IR** (ATR, 32 scans, cm^{-1}): 3051 (w), 2950 (w), 2895 (w), 2844 (w), 2791 (w), 2729 (w), 2167 (w), 2140 (w), 2102 (w), 1946 (w), 1770 (s), 1581 (m), 1560 (m), 1509 (w), 1475 (s), 1434 (w), 1372 (w), 1349 (w), 1322 (w), 1267 (w), 1157 (w), 1079 (w), 1070 (w), 1024 (w), 991 (w), 964 (w), 937 (w), 901 (w), 851 (w), 781 (w), 748 (s), 701 (s), 632 (m), 513 (s), 451 (s). **Elemental analysis** calcd (%) for M($C_{15}H_{10}Li_2$) = 204.13 g mol^{-1}: C 88.26, H 4.94; found: C 87.34, H 4.66.

Synthesis of complex 2b. The purple [*rac*-(ebthi)$TiCl_2$] (0.67 mmol, 259 mg, 1 eq) and compound **1b** [$Li_2(PhC_3Ph)$] (0.96 mmol, 210 mg, 1.4 eq) were mixed and dissolved in toluene (30 mL) at room temperature. Then the reaction mixture was stirring for two hours at room temperature, the deep purple solution was cannula-filtered. The toluene solution was concentrated and stored at -78 °C for crystallisation to obtain complex **2b** as dark red crystals (107.7 mg, 32%). **^{1}H NMR** (25 °C, [D6]benzene, 400.20 MHz): δ = 7.44–7.38 (dd, 4H Ph), 7.35–7.26 (t, 4H Ph), 7.06–7.00 (t, 2H Ph), 6.68 (d, 2H, C*H* ebthi), 5.64 (d, 2H, C*H* ebthi), 2.73–2.58 (m, 4H, 2 x CH_2 ebthi), 2.05–1.95 (m, 4H, 2 x CH_2 ebthi), 1.93–1.77 (m, 2H, CH_2 ebthi), 1.43–1.03 (m, 10H, 5 x CH_2 ebthi). **^{13}C NMR** (25 °C, [D6]benzene, 100.63 MHz): δ = 211.9 (*C*=C=*C*), 141.4 (2 x *C* Ph), 130.1, 128.9, 126.6 (10 x *C*H Ph), 123.5, 123.2 (4 x *C* ebthi), 119.3 (C=*C*=C), 118.6 (2 x *C* ebthi), 115.4, 99.4 (4 x *C*H ebthi), 27.5, 24.1, 24.0, 22.9, 22.9 (10 x *C*H_2 ebthi). **MS-CI$^+$** (*isobutane*): [(M-ebthi-Ti-PhH)$^+$] 92 (100), [(M+H)$^+$] 503 (5), [(M-PhCCCPh)$^+$] 312 (23). **IR** (ATR, 32 scans, cm^{-1}): 3053 (w), 3023 (w), 2920 (m), 2850 (w), 2097 (w), 1971 (w), 1880 (w), 1790 (w), 1717 (w), 1583 (w), 1562 (w), 1478 (w), 1437 (m), 1376 (w), 1346 (w), 1280 (w), 1238 (w), 1185 (w), 1138 (w), 1066 (w), 1025 (w), 1003 (w), 952 (w), 903 (w), 876 (w), 784 (m), 753 (s), 725 (s), 690 (s), 641 (m), 620 (m), 584 (s), 539 (m), 507 (m), 464 (m). **Elemental analysis** calcd (%) for M($C_{35}H_{34}Ti$) = 502.52 g mol^{-1}: C 83.65, H 6.82; found: C 82.79, H 6.42.

Synthesis of complex 3b. The pale yellow [*rac*-(ebthi)$ZrCl_2$] (0.31 mmol, 134 mg, 1.0 eq) and compound **1b** [$Li_2(PhC_3Ph)$] (0.44 mmol, 96 mg, 1.4 eq) were mixed and dissolved in toluene (20 mL) at 0 °C. Then the reaction mixture was stirring for one hour at 0 °C, the deep green solution was cannula-filtered. During the concentration of toluene solution, the solid precipitated from the solution. After removing all volatiles in vacuum, pentane was used to wash the solid (3 x 5 mL), yielding complex **3b** as a green solid (30.5 mg, 18%). Single crystals suitable for SC-XRD analysis were grown from toluene at -78 °C. **^{1}H NMR** (25 °C, [D6]benzene, 400.20 MHz): δ = 7.55–7.49 (dd, 4H Ph), 7.34–7.29 (t, 4H Ph), 7.11–7.06 (t, 2H Ph), 6.36 (d, 2H, CH ebthi), 5.66 (d, 2H, CH ebthi), 2.74–2.63 (m, 4H, 2 x CH_2 ebthi), 2.30–2.16 (m, 4H, 2 x CH_2 ebthi), 2.07–2.00 (m, 2H, CH_2 ebthi) , 1.66–1.17 (m, 10H, 5 x CH_2 ebthi). **^{13}C NMR** (25 °C, [D6]benzene, 100.63 MHz): δ = 186.5 (C=C=C), 142.7 (2 x C Ph), 139.8 (C=C=C), 130.1, 128.9 (8 x CH Ph), 126.5 (2 x CH Ph), 123.8, 123.8, 120.2 (6 x C ebthi), 114.6, 101.8 (4 x CH ebthi), 27.3, 24.0, 23.9, 23.3, 23.2 (10 x CH_2 ebthi). **MS-CI$^+$** (isobutane): [(M-H)$^+$] 544 (41), [(M-ebthi-Zr)$^+$] 192 (100). **IR** (ATR, 32 scans, cm^{-1}): 3050 (w), 3022 (w), 2917 (w), 2852 (w), 2251 (w), 2087 (w), 1939 (w), 1872 (w), 1712 (m), 1583 (w), 1562 (w), 1491 (w), 1478 (w), 1431 (m), 1373 (w), 1346 (w), 1330 (w), 1278 (w), 1240 (w), 1186 (w), 1170 (w), 1140 (w), 1065 (w), 1024 (w), 1001 (w), 979 (w), 965 (w), 952 (w), 904 (w), 860 (w), 791 (s), 752 (s), 729 (m), 689 (s), 649 (m), 622 (m), 595 (s), 535 (m), 507 (m), 465 (w), 421 (m), 405 (m). **Elemental analysis** calcd (%) for M($C_{35}H_{34}Zr$) = 544.17 g mol^{-1}: C 77.01, H 6.28; found: C 72.16, H 5.83.

Synthesis of complex 1c. A solution of n-BuLi (6.9 mmol, 2.8 mL, 2.5 M n-hexane solution, 2.1 eq,) was added dropwise within 20 min to a colourless solution of 1-(trimethylsilyl)-3-phenylprop-1-yne (3.3 mmol, 619 mg, 1.0 eq) in benzene (10 mL) at room temperature. The clear pale-yellow solution was cooled to -78 °C, degassed and heated to 50 °C for two days. During this time a yellow solid appeared. The solution was cannula-filtered, and the yellow solid was then washed with n-hexane (3 x 10 mL), dried in vacuum for three hours to obtain **1c** as a yellow solid (421 mg, 64%). Single crystals suitable for SC-XRD analysis were grown from THF/n-hexane at -78 °C. Note: This compound is highly sensitive and undergoes degradation into unknown organolithium compounds. Freshly prepared samples can however be used for the synthesis of metallacycles. **^{1}H NMR** (25 °C, [D6]benzene, 400.20 MHz): δ = 6.96-6.85 (d, 2H Ph), 6.64-6.54 (t, 2H Ph), 6.08-5.97 (t, 1H Ph), 0.02 (s, 9H, $SiMe_3$). **^{13}C NMR** (25 °C, [D6]benzene, 100.63 MHz): δ = 159.4 (C=C=C), 129.2 (C Ph), 128.2 (2 x CH Ph), 128.0 (CH Ph), 126.5 (2 x CH Ph), 120.0 (C=C=C-$SiMe_3$), 113.1 (Ph-C=C=C), 4.70 (3 x CH_3 $SiMe_3$). **^{29}Si NMR** (25 °C, [D6]benzene, 79.49 MHz): δ = -23.3, **^{7}Li NMR** (25 °C, [D8]THF, 155.51 MHz): δ = 0.65 (s), 0.05 (s). **MS-CI$^+$** (isobutane): [(2M-4Li)$^+$] 373 (38), [(M-2Li+Ph-2H)$^+$] 261 (100), [(M-2Li+2H)$^+$] 189 (50), [$SiMe_3^+$] 73 (97). **IR** (ATR, 32 scans, cm^{-1}): IR (ATR, neat, cm-1): 3056 (w), 2947 (w), 2889 (w), 2096 (w), 1861 (m), 1824 (m), 1779 (m), 1576 (m), 1548 (w), 1469 (m), 1399 (w), 1296 (w), 1241 (m), 1174 (w), 1111 (w), 1067 (w), 1025 (w), 986 (w), 829 (s), 777 (w), 748 (s), 697 (m), 646 (w), 618 (w). **Elemental analysis** calcd (%) for M($C_{12}H_{14}Li_2Si$) = 200.21 g mol^{-1}: C 71.99, H 7.05; found: C 69.31, H 6.86.

Synthesis of complex 2c. The purple [*rac*-(ebthi)$TiCl_2$] (0.3 mmol, 151 mg, 1.0 eq) and compound **1c** [$Li_2(PhC_3SiMe_3)$] (0.3 mmol,60 mg, 1.0 eq) were mixed and dissolved in benzene (20 mL) at room temperature. The reaction mixture was stirred for one hour at same conditions. The deep red solution was cannula-filtered and the filtrate was dried in vacuum for three hours to obtain complex **2c** as a dark brown solid (80.5 mg, 50%). **^{1}H NMR** (25 °C, [D6]benzene, 400.20 MHz): δ = 7.32-7.18 (m, 4H Ph), 6.98 (d, 1H CH ebthi), 6.95-6.88 (t, 1H Ph), 6.78 (d, 1H, CH ebthi), 5.54 (d, 1H, CH ebthi), 5.41 (d, 1H, CH ebthi), 2.69-2.59 (m, 4H, 2 x CH$_2$ ebthi), 2.35–1.98 (m, 4H, CH$_2$ ebthi), 1.71–1.49 (m, 4H, 2 x CH$_2$ ebthi) , 1.31-1.88 (m, 8H, CH$_2$ ebthi), 0.39 (s, 9H, SiMe$_3$). **^{13}C NMR** (25 °C, [D6]benzene, 100.63 MHz): δ = 216.1 (Ph-C=C=C), 207.1 (C=C=C-SiMe$_3$), 126.3 (C=C=C), 143.1 (C Ph), 128.8 (2 x CH Ph), 128.5 (2 x CH Ph), 125.4 (CH Ph), 123.7, 123.5, 123.3, 123.2, 118.0, 118.0 (6 x C ebthi), 117.2, 115.5, 100.0, 99.5 (4 x CH ebthi), 24.2, 24.2, 23.9, 23.8, 23.1, 22.9, 22.8, 22.8 (8 x CH$_2$ ebthi), 2.3 (3 x CH$_3$ SiMe$_3$). **^{29}Si NMR** (25 °C, [D6]benzene, 79.49 MHz): δ = -9.75. **MS-CI$^+$** (isobutane): [(M-C$_2$SiMe$_3$)$^+$] 401 (54), [(M-Ti-C$_3$PhSiMe$_3$+H)$^+$] 265 (36), [(M-Ti-ebthi+2H)$^+$] 189 (13), [(CPh+2H)$^+$] 91 (67), [(Ph+2H)$^+$] 79 (46), [SiMe$_3$$^+$] 73 (30), [(SiMe$_3$-4H)$^+$] 69 (100). **IR** (ATR, 32 scans, cm^{-1}): 3058 (w), 3022 (w), 2926 (m), 2852 (m), 2564 (w), 2453 (w), 2163 (w), 2102 (w), 1915 (w), 1840 (w), 1799 (w), 1730 (w), 1594 (w), 1491 (w), 1442 (w), 1374 (w), 1347 (w), 1285 (w), 1244 (m), 1188 (w), 1122 (w), 1069 (w), 1032 (w), 1004 (w), 953 (w), 934 (w), 902 (w), 836 (s), 783 (m), 754 (s), 723 (m), 694 (s), 644 (m), 622 (w), 585 (w), 541 (w), 509 (w), 469 (w), 442 (w), 411 (w). **Elemental analysis** calcd (%) for M(C$_{28}$H$_{38}$SiTi) = 498.61 g mol^{-1}: C 77.09, H 7.68; found: C 76.39, H 7.35.

Synthesis of complex 3c. The pale yellow [*rac*-(ebthi)ZrCl$_2$] (0.15 mmol, 64 mg) and compound **1c** [Li$_2$(PhC$_3$SiMe$_3$)] (0.15 mmol, 30 mg) were mixed and dissolved in benzene (20 mL) at room temperature. The reaction mixture was stirred for one hour at same conditions. The deep green solution was cannula-filtered and the filtrate was dried in vacuum for three hours to obtain complex **3c** as a green solid (15.6 mg, 19%). **^{1}H NMR** (25 °C, [D6]benzene, 400.20 MHz): δ = 7.37-7.24 (m, 4H Ph), 7.05-6.97 (t, 1H Ph), 6.83 (d, 1H CH ebthi), 6.61 (d, 1H, CH ebthi), 5.59 (d, 1H, CH ebthi), 5.47 (d, 1H, CH ebthi), 2.66 (s, 4H, 2 x CH$_2$ ebthi), 2.42–2.28 (m, 2H, CH$_2$ ebthi), 2.26–2.00 (m, 4H, 2 x CH$_2$ ebthi) , 2.20-2.18 (m, 2H, CH$_2$ ebthi), 1.70-1.40 (m, 4H, 2 x CH$_2$ ebthi), 1.40-1.14 (m, 4H, 2 x CH$_2$ ebthi), 0.42 (s, 9H, SiMe$_3$). **^{13}C NMR** (25 °C, [D6]benzene, 100.63 MHz): δ = 177.7 (Ph-C=C=C), 176.8 (C=C=C-SiMe$_3$), 145.7 (C=C=C), 144.2 (C Ph), 128.8 (2 x CH Ph), 128.7 (2 x CH Ph), 124.9 (CH Ph), 124.5, 124.4, 123.8, 123.2, 119.8, 119.7 (6 x C ebthi), 116.0, 113.0, 102.0, 101.8 (4 x CH ebthi), 27.4, 27.2, 24.2, 23.9, 23.6, 23.1, 23.0, 22.7 (8 x CH$_2$ ebthi), 2.4 (3 x CH$_3$ SiMe$_3$). **^{29}Si NMR** (25 °C, [D6]benzene, 79.49 MHz): δ = -10.16. **MS-CI$^+$** (isobutane): [(M-CSiMe$_3$-H)$^+$] 455 (8), [(M-Zr-C$_3$PhSiMe$_3$+3H)$^+$] 267 (100), [SiMe$_3$$^+$] 73 (3). **IR** (ATR, 32 scans, cm^{-1}): 3019 (w), 2926 (w), 2850 (w), 2166 (w), 1900 (w), 1856 (w), 1780 (w), 1725 (w), 1591 (w), 1492 (w), 1439 (w), 1374 (w), 1316 (w), 1244 (w), 1177 (w), 1153 (w), 1099 (w), 1069 (w), 1031 (w), 1005 (w), 930 (w), 834 (w), 778 (w), 754 (w), 690 (w), 648 (w), 625 (w), 603 (w), 543 (w), 507 (w), 466 (w), 404 (w). **Elemental analysis** calcd (%) for M(C$_{28}$H$_{38}$SiZr) = 541.97 g mol^{-1}: C 70.92, H 7.07; found: C 63.91, H 5.78.

Supporting Information

The authors have cited additional references within the Supporting Information.[42-61] Deposition Number(s) 2311081 (for **1b**), 2311082 (for **1c**), 2311083 (for **2b**), 2311084 (for **3b**), 2311085 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe http://www.ccdc.cam.ac.uk/structures.

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RESEARCH ARTICLE

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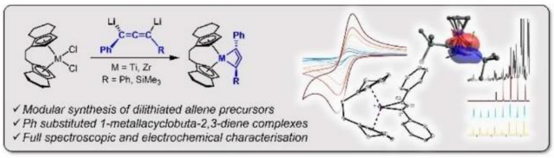

Ring-substituted 1-metallacyclobuta-2,3-dienes were prepared from suitable organolithium precursors. The effect of introduction of phenyl groups was studied using a combination of experimental and theoretical methods. For the first time cyclic voltammetry, EPR, and solid state NMR spectroscopy were used to support structural and DFT data.

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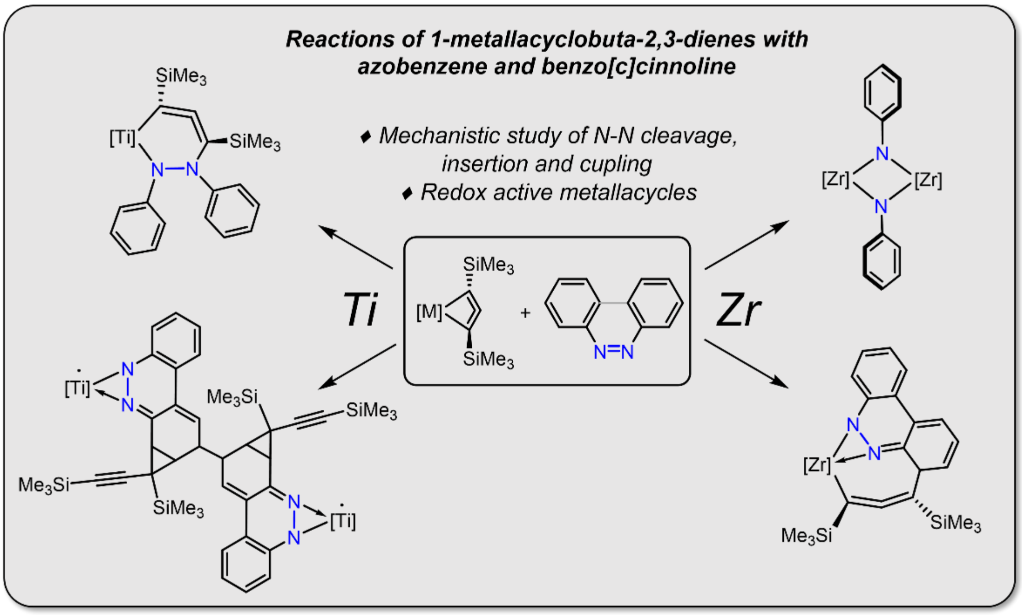
4.4 Reactions of group 4 1-metallacyclobuta-2,3-diene complexes with diazenes: N=N bond cleavage vs. N-C bond formation and dearomatization

Sihan Li, Mirjam Schröder, Xinzhe Shi, Anke Spannenberg, Jörg Fischer, Björn Corzilius, Fabian Reiß and Torsten Beweries.

Manuscript submitted.

Contribution to this paper is 80%.



Reactions of group 4 1-metallacyclobuta-2,3-diene complexes with diazenes: N=N bond cleavage vs. N-C bond formation and dearomatization

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Reactions of group 4 1-metallacyclobuta-2,3-diene complexes with diazenes: N=N bond cleavage vs. N-C bond formation and dearomatization

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ABSTRACT: Reactions of two [*rac*-(ebthi)Ti] and [*rac*-(ebi)Zr] based 1-metallacyclobuta-2,3-diene complexes with diazenes are described. With azobenzene, cleavage of the N=N bond is observed in case of Zr, leading to the formation of a dinuclear Zr(IV) imido complex **1**. In contrast, insertion of azobenzene into the Ti-C bond of the titanacycle produces a six-membered aza-metallacycle **6**, which could only be characterized by NMR spectroscopy. With geometrically restricted benzo[*c*]cinnoline, activation and dearomatization of the phenyl group of the substrate occurs, leading to formation of unusual mono- (M = Zr, **3**) and dinuclear complexes (M = Ti, **7**). Reaction mechanisms leading to the formation of these unusual complexes are proposed based on control experiments.

INTRODUCATION

The coordination and activation of azo-compounds at transition metal fragments have received much attention because of the great potential of resulting imido- and hydrazido complexes in catalysis,[1] nitrogen fixation[2] and atom and group transfer processes.[3] The reactivity of these compounds is strongly dependent on the electronic nature and steric profile of the respective organometallic species, leading to either coordination or insertion of the diazene, reduction of the coordinated substrate, or cleavage of the N-N bond (Figure 1).[4] Most of the studies on the activation of N-N bonds on azo-compounds were carried out using low-valent early transition metals and azobenzene, or the geometry-restricted analog benzo[*c*]cinnoline (BCC) as model substrates. In many cases, metallic reducing agents are used.[5] Reports of reactions of mid- or high-valent transition metal complexes are comparably rare.[6]

In the past, metallacycles have been interesting platforms to study the coordination and activation of a variety of small molecules, such as nitriles,[7] isocyanides,[8] carbodiimides[9] as well as alkyl imines.[10] We have recently reported group 4 metallocene based 1-metallacyclobuta-2,3-dienes $L_nM(RC_3R)$ (L_nM = *ansa*-metallocene, M = Ti, Zr; R = $SiMe_3$, Ph), unique small ring-strained metallacycles.[11] In the case of Ti these compounds possess biradical character with antiferromagnetically coupled electrons on the Ti(III) center and the formal allenylide C_3 unit of the metallacycle.[9,11a] The Zr compounds are better described as Zr(IV) species with a covalently bound dianionic allenediide ligand. In this case aliphatic C-H activation at non-Cp containing alkyl groups was observed, producing new types of tucked-in complexes.[9,11b]

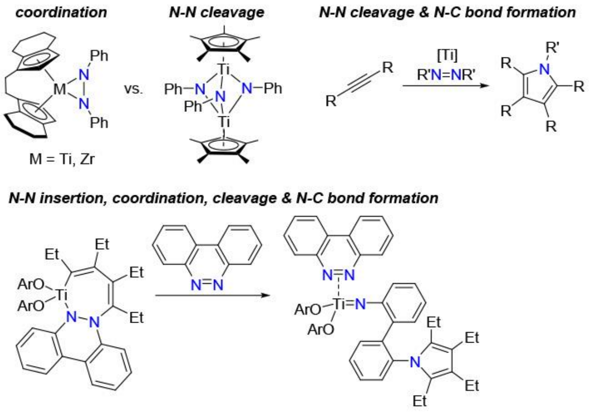
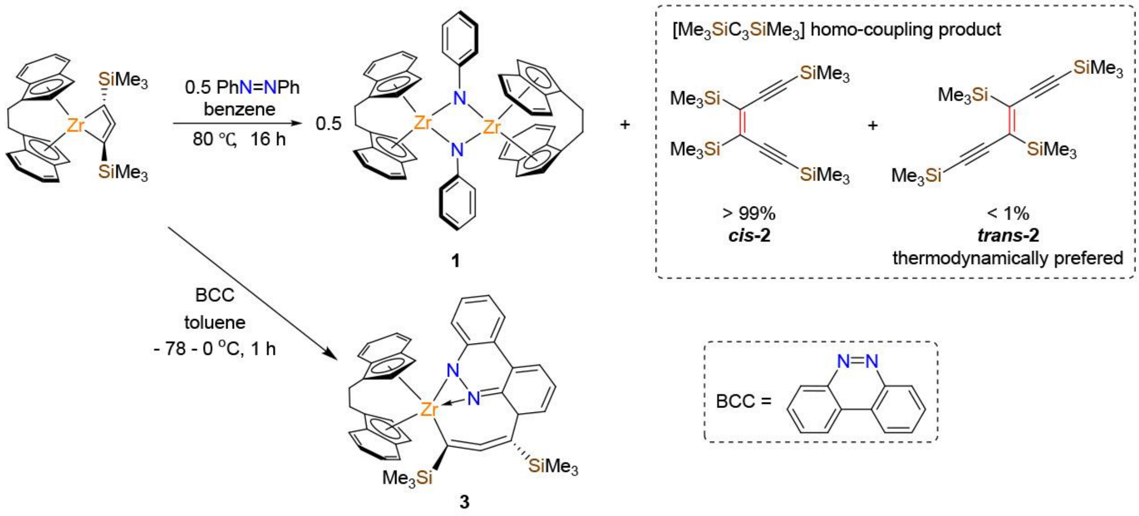


Figure 1. Selected examples of coordination vs. activation of diazenes at transition metal centers.[3a,4d,6c]

Scheme 1. Synthesis of Zr imido complex 1 and compound *cis*-2.



More recently, Mindiola and co-workers have reported NacNac-based 1-metallacyclobuta-2,3-dienes (M = Ti, V) as key intermediates in the catalytic production of *cyclo*-polyalkynes, forming the catalytically active alkylidene species.[12] Apart from this, the organometallic reactivity of the metallocene-based complexes was limited to simple insertion, e.g., of carbonyl compounds and carbodiimides, into the M-C bonds, followed by retro-cycloaddition or rearrangement reactions, independent of the metal used.

To evaluate the behavior of electronically different, yet structurally related complexes and extend the scope of reactivity to potentially redox-active substrates, we have now used two 1-metallacyclobuta-2,3-diene complexes to investigate the reactivity of this class of compounds towards the diazenes azobenzene and benzo[*c*]cinnoline. First indications of the redox non-innocence of the C_3 ligand of 1-metallacyclobuta-2,3-dienes were recently obtained in electrochemical investigations of the *rac*-(ebthi)-based Ti and Zr complexes.[13] In this contribution, we describe a diverse reactivity ranging from simple M-N coordination to N-N double bond cleavage of the azobenzene, N-C coupling and dearomatization of the diazene substrates.

RESULTS AND DISCUSSION

Reactions of 1-zirconacyclobuta-2,3-diene with diazenes. We previously reported the instability of the η5-indenyl complex [*rac*-(ebi)Ti($Me_3SiC_3SiMe_3$)] (ebi = 1,2-ethylene-1,1′-bis(η5-indenyl), resulting in formation of the organic coupling product *trans* $Me_3SiC{\equiv}C{-}C(SiMe_3){=}C(SiMe_3){-}C{\equiv}CSiMe_3$ (***trans*-2**), likely caused by the relatively high biradical character of this Ti species.[9] Furthermore, intramolecular C-H activation of the η5-tetrahydroindenyl complex [*rac*-(ebthi)Zr($Me_3SiC_3SiMe_3$)] (ebthi = 1,2-ethylene-1,1′-bis(η5-tetrahydroindenyl))[11b], complicated the study of its reactivity. To avoid the influence of these factors on reactivity, we selected the related complexes [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)] and [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] that can readily be isolated in pure form.

[*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] reacts with azobenzene in 2:1 ratio at 80 °C in benzene, leading to the formation of a black precipitate, which was identified as the dinuclear Zr(IV) imido complex **1**, in 87% isolated yield (Scheme 1). Complexes of group 4 metals with bridging imido ligands were reported on several occasions, e.g. by reactions with amines[14] or by cleavage of diazenes.[15a] Of note, no conversion was observed at room temperature. ^1H NMR spectra of compound **1** support the highly symmetric nature of this species. Furthermore, the absence of the signals at 0 – 0.5 ppm indicates the cleavage of the metallacyclic unit and dissociation of the [$Me_3SiC_3SiMe_3$] fragment. Crystals of **1** were grown from a concentrated benzene solution at room temperature and the solid-state structure was determined by single crystal X-ray diffraction (SC-XRD) analysis (Figure 2 The N···N distance is 2.72 Å, confirming the complete cleavage of the N-N double bond of PhN=NPh (*c.f.* d(N-N) = 1.42 Å)[16] The two *rac*-(ebi) ligands form a pocket around the central Zr_2N_2 four-membered ring. The Zr-N(imido) bond lengths are in the range of Zr-N single bonds. The bond angles in the Zr_2N_2 ring, at Zr1, Zr2, N1 and N2 are similar to those found in the complex {[NNNq]ZrCl(μ2-*p*-$NC_6H_4{}^tBu$)}2 reported by Heyduk and co-workers (NNNq = bis(2-isopropylamido-4-methoxyphenyl)amide ligand in quinonate form).[15b] Furthermore, with the help of

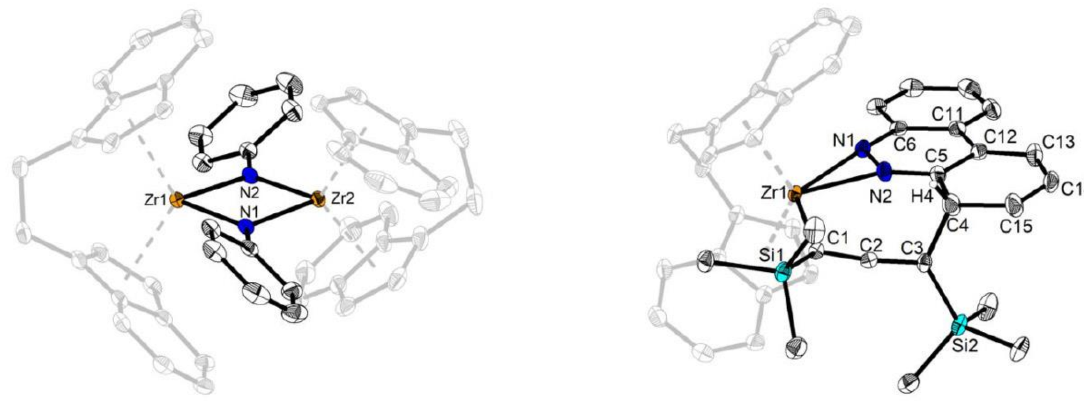


Figure 2. Molecular structure of complex **1** and **3**. Thermal ellipsoids correspond to 30% probability. The [*rac*-(ebi)] ligand is shown in grey, hydrogen atoms (expect H4 in complex **3**) and solvent (benzene in complex **1**, toluene in complex **3**) are omitted for clarity. Selected bond distances (Å) and angles (deg): complex **1**: Zr1-N1 2.072(2), Zr1-N2 2.130(2), Zr2-N1 2.109(2), Zr2-N2 2.070(2), Zr1···Zr2 3.18, N1-Zr1-N2 80.79(8), N1-Zr2-N2 81.34(8), Zr1-N1-Zr2 99.18(9), Zr1-N2-Zr2 98.59(9); complex **3**: Zr1-N1 2.2118(19), Zr1-N2 2.2175(19), Zr1-C1 2.349(2), N1-N2 1.355(3), N1-C6 1.370(3), N2-C5 1.314(3), C1-C2 1.290(3), C2-C3 1.336(3), C3-C4 1.542(4), C4-C5 1.526(4), N1-Zr1-N2 35.63(7), Zr1-N1-N2 72.41(12), N1-N2-Zr1 71.95(11), C1-C2-C3 172.6(2), C3-C4-C5 107.0(2), C3-C4-C15 114.5(2), C5-C4-C15 109.9(2).

PLATON[17], we identified four weak π-π stacking interactions between the two phenyl rings and their neighboring six membered rings of the *rac*-(ebi) ligands (centroid-centroid distances range between 3.758(2) and 3.977(2) Å, for further details see supporting information Table S3 and Figure S52). These beneficial interactions are also supported by the Interaction Region Identifier Analysis (IRI analysis, Figure S60)[18].

In previous studies of 1-metallacyclobuta-2,3-dienes, the eliminated C_3 ligand of the former metallacycle underwent homocoupling to produce ***trans*-2**[9,11] (for this compound the *trans* isomer is thermodynamically preferred by $\Delta G_{trans\text{-}cis}$ = -40.63 kJ mol-1). To our surprise, in the present case this homocoupling product is present as the *cis* isomer as major product (***cis*-2**) in over 99% yield (calculated from ^{1}H NMR spectra), with two singlet signals at δ 0.29 and 0.27 ppm in ^{1}H NMR. Only traces of ***trans*-2** were observed during the reaction (Figure S1). Compound ***cis*-2** can be isolated from combined and concentrated washing solutions by column chromatography.

Next, the reactivity between geometry-restricted BCC and [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] was studied. BCC reacts with [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] in 1:1 ratio to form complex **3** in toluene. This product complex is not stable in solution and slowly decomposes within a few hours at room temperature (Figure S2). To minimize this decomposition, the reaction was carried out at -78 °C and slowly warmed to 0 °C. Crystals suitable for SC-XRD analysis were obtained from toluene at -30 °C. In the molecular structure of complex **3**, bond distances C3-C4 1.542(4), C4-C5 1.526(4) and C4-C15 1.519(4) Å are in the range of C(sp^3) - C(sp^3) single bonds, indicating a dearomatization of the arene unit coupled to the intact allene group (C1-C2 1.290(3), C2-C3 1.336(3) Å). As a consequence, N-C bond distances are significantly different (N1-C6 1.370(3), N2-C5 1.314(3) Å). This is also supported by ^{1}H-^{13}C HSQC NMR analysis, which shows a resonance for the proton at C4 at 4.84 ppm, correlating to a ^{13}C resonance at 47.1 ppm.

To compare the reactivity of azobenzene with structurally related [*rac*-(ebi)Zr] complexes of different oxidation states, we synthesized the previously unknown zirconocene bis(trimethylsilyl)acetylene complex ***rac*-4** (Scheme 2). This species can be conveniently prepared using [*rac*-(ebi)$ZrCl_2$] and lithium as a reductant in presence of bis(trimethylsilyl)acetylene (btmsa) in benzene at 60 °C for eight days. ***rac*-4** can be obtained as golden yellow crystals in 89% isolated yield (see Supporting Information for details). It should be noted that when choosing toluene as solvent instead of benzene, formation of ***rac*-4** as well as ***meso*-4** (green crystals) occurs in 3:7 ratio.

When treating complex ***rac*-4** with azobenzene in benzene at room temperature, the color of the reaction mixture turns from yellow to dark green immediately, affording the diazo complex [*rac*-(ebi)Zr(η^2-PhNNPh)] (**5**, Scheme 2) as a black solid in 67% isolated yield, as well as free btmsa (^{1}H: δ = 0.16 ppm[19]). Brown-black crystals of **5** were grown from a concentrated benzene solution at room temperature. The SC-XRD analysis (Figure S55) shows the diazene in side-on coordination, similar to previous studies of related systems.[4d] The N-N distance is 1.439(3) Å, in the range of a N-N single bond in organic compounds with nitrogen atoms in a pyramidal geometry. The N-Zr-N angle is 40.42(8) °, close to values in the similar complex *rac*-(ebthi)Zr(η^2-PhNNPh) reported by Rosenthal and co-workers.[4d]

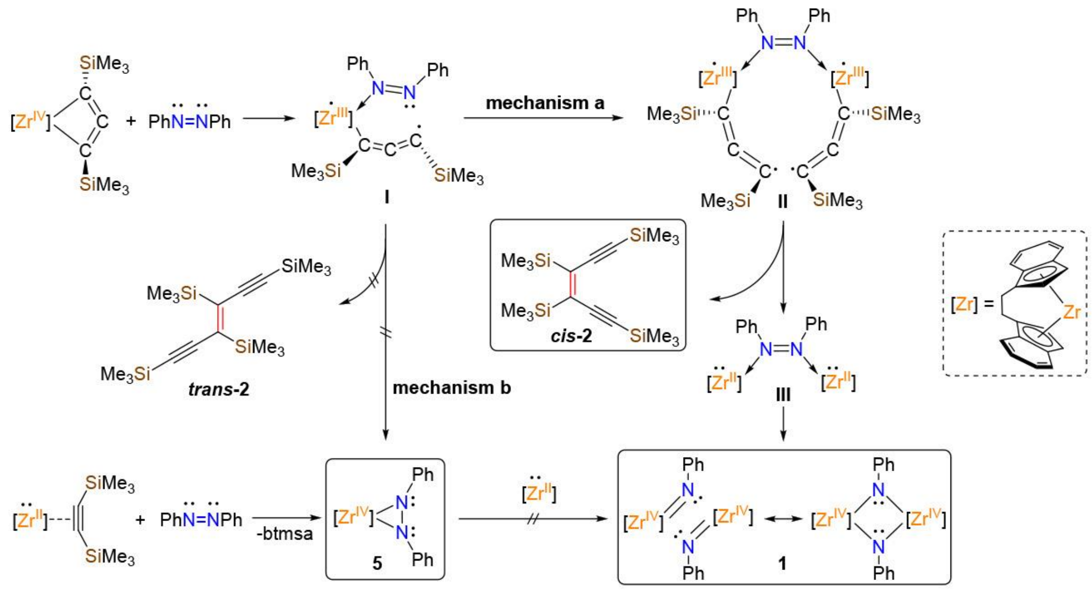
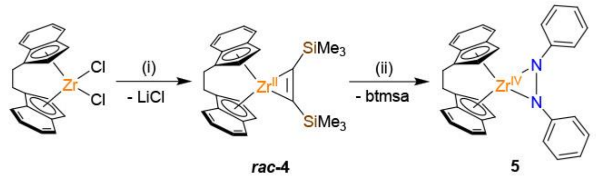


Figure 3. Possible mechanisms for the cleavage of PhN=NPh and formation of **1** and ***cis*-2**.

Scheme 2. Synthesis of complexes *rac*-4 and 5. Reaction conditions: (i) Li, btmsa, benzene, 60 °C, 8 days; (ii) PhN=NPh, benzene, room temperature, 10 min.

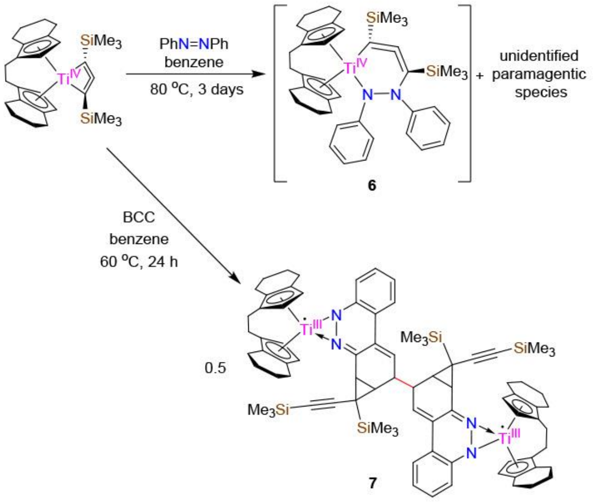


Taken together, these results suggest that the type of reaction product is affected by the oxidation state of the Zr center and the nature of the metallacycle, resulting in coordination or cleavage of the diazenes. Whereas the formation of **5** can be readily rationalized by simple exchange of neutral π-ligand followed by a two electron transfer from the Zr(II) center to the NN unit, the reaction mechanism leading to N-N cleavage in **1** is likely to be more complex. We propose two possible reaction pathways (Figure 3), both induced by η^1-coordination of azobenzene to the Zr(IV) center as it was reported for L-type ligands on numerous occasions before.[20] Along with this, homolytic cleavage of one Zr-C$_{\text{allene}}$ bond is proposed which is in line with the formation of **3**. Subsequently, coordination of a second Zr to the vacant N donor could produce a dinuclear species (intermediate **II**) in which two C_3 ligands undergo coupling to furnish a coordinated diallene ligand.

Elimination of the latter would result in formation of ***cis*-2** only, under the influence of steric hindrance from two [*rac*-ebi] ligands, and a coordinatively unsaturated dinuclear diazene bridged Zr(II) complex (intermediate **III**). Species **III** could undergo cleavage/reduction of the N-N unit to yield complex **1** as bis-Zr(IV) imido complex (mechanism **a**). Alternatively, cleavage of the C_3 ligand could produce an η^2-coordinated diazene complex which could dimerize with additional zirconocene [*rac*-(ebi)Zr(II)] to produce the dinuclear imido species **1**. To evaluate this path, two control experiments were carried out. i) The reaction of two equivalents of ***rac*-4** with azobenzene at 80 °C was investigated. Initially, **5** was formed and one equivalent of ***rac*-4** remained unreacted in solution. This 1:1 mixture was further heated at 80 °C for 20 hours, but no reaction took place (Figure S3), indicating that mechanism **b** is unlikely. ii) The reaction of **5** with one equivalent of [rac-(ebi)Zr(Me$_3$SiC$_3$SiMe$_3$)] at 80 °C for 16 h was investigated. However, both complexes remained unchanged, and no reaction took place (Figure S4). Both results suggest that once complex **5** formed, it shows a high thermal stability and does not react with further [Zr(II)] species. These results, combined with the exclusive presence of ***cis*-2**, support that intermediates **II** and **III** are indispensable in this reaction.

Reactions of 1-titanacyclobuta-2,3-diene with diazenes. To compare the reactivity of Ti and Zr complexes, we have next studied the reaction of [*rac*-(ebthi)Ti(Me$_3$SiC$_3$SiMe$_3$)] with azobenzene. Initial experiments that were performed at room temperature showed no conversion. Heating at 80 °C for three days with a 1:1 stoichiometry of Ti complex and diazene showed residual azobenzene by ^{1}H NMR spectroscopy (Figure S5). Variation of the ratio of Ti/azobenzene to 2:1 and repeating the reaction under same conditions resulted in full conversion of both starting materials (Figure S6), allowing for the isolation of a black solid in 33% yield. ^{1}H NMR analysis of this material shows four characteristic doublets at δ 6.62, 6.30, 5.41 and 5.30 ppm, assigned to Cp protons, which indicate a C_1-symmetric structure. The ratio between the protons of the phenyl and SiMe$_3$ groups suggest the presence of both, diazene and allenediide fragments. Also, based on ^{1}H and ^{13}C NMR spectroscopy, no evidence for dearomatization of the phenyl group could be found. Based on these NMR data, and mass spectrometry, showing a molecular ion peak at m/z 676, we suggest the formation of a 1,2-insertion product **6** (Scheme 3).

Scheme 3. Synthesis of complexes 6 and 7.



Interestingly, ¹H NMR monitoring of the formation of **6** shows a significant decrease in signal intensity, likely due to formation of paramagnetic by-products. This assumption could be corroborated using Evans method (Figure S7), providing further evidence why reactions in 1:1 stoichiometry do not show full conversion of both starting materials. Unfortunately, neither crystals for further structural characterization of compound **6** nor of the unclear paramagnetic complex could be obtained.

The reaction of [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)] with BCC in 1:1 ratio in benzene at 60 °C results in a color change from purple to red. ¹H NMR monitoring of this reaction shows complete decay of the resonances of both starting materials after one day (Figure S8), suggesting the presence of paramagnetic Ti(III) species. Orange crystals of a new species **7** were isolated in 87% yield after removal of all volatiles in vacuum and extraction with hot hexane. (Scheme 3). The molecular structure (Figure 4) of complex **7** shows a dinuclear Ti(III) complex with two η^2-coordinated BCC units that connect the metal centers by dimerization. In addition, the former C_3 units of the 1-titanacyclobuta-2,3-diene are cyclopropanated to these BCC moieties. The bond distance C9-C24 of 1.556(3) Å indicates the presence of a new C-C single bond (C-C Σr_{cov} = 1.50 Å[21]). Both units of the dinuclear assembly are found in *gauche* conformation with a torsion angle of C8-C9-C24-C25 73.8(3)°, and the dihedral angle between two BCC planes is 52.4°. Non-symmetric Ti-N coordination of the former BCC ligand is evident from differences in Ti-N and C-N bond distances, averaged over both halves of the molecule ($Ti\text{-}N_{covalent}$ 2.054, $Ti\text{-}N_{dative}$ 2.145, $C\text{-}N_{single}$ 1.371, $C\text{-}N_{double}$ 1.305 Å), supporting the dearomatization of this fragment.

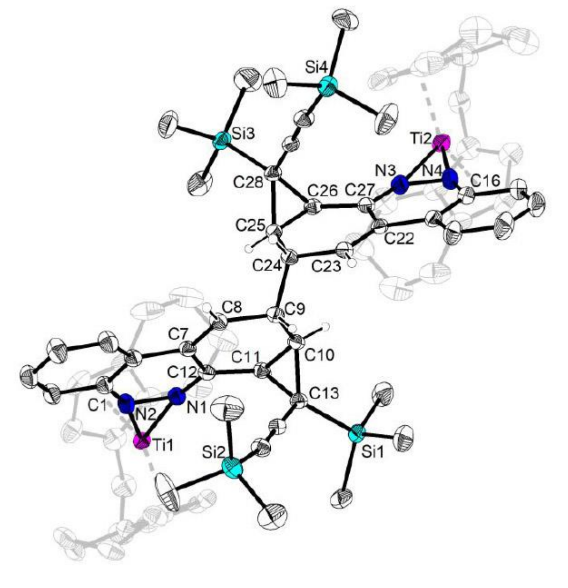


Figure 4. Molecular structure of complex **7**. Thermal ellipsoids correspond to 30% probability. The [*rac*-(ebthi)] ligands are shown in grey and hydrogen atoms (except H8-11, H23-26), minor occupied parts of the disorder and solvent (hexane) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1-N1 2.144(2), Ti1-N2 2.054(2), N1-N2 1.357(3), N2-C1 1.365(4), N1-C12 1.303(3), C12-C7 1.451(4), C7-C8 1.347(4), C8-C9 1.506(4), C9-C10 1.516(4), C10-C11 1.505(4), C11-C12 1.477(4), C10-C13 1.541(4), C11-C13 1.553(4), C9-C24 1.556(3), Ti2-N3 2.146(2), Ti2-N4 2.054(3), N3-N4 1.355(4), N3-C27 1.306(4), N4-C16 1.376(4), C22-C23 1.344(4), C23-C24 1.496(4), C24-C25 1.519(4), C25-C26 1.498(4), C26-C27 1.472(4), C27-C22 1.455(4), C25-C28 1.535(4), C26-C28 1.559(4), N1-Ti1-N2 37.65(9), N3-Ti2-N4 37.57(10), C8-C9-C24 110.9(2), C10-C9-C24 111.3(2), C8-C9-C10 113.7(2).

To elucidate the electronic structure of the molecule, temperature-dependent X-band EPR measurements of a solution of **7** in toluene were conducted (Figure S57). In liquid state, the dimer yields a nearly isotropic signal with no hyperfine couplings visible, despite the very close proximity of each Ti atom to two nitrogens. The g-value of $g = 1.985$ suggests a Ti centered radical. The singly occupied molecular orbitals SOMO and SOMO-1 of **7** at the UB3LYP[22]-D3[23]/def2-TZVP[24] level of theory (SOMO Figure 5a, middle; SOMO-1 Figure S63) differ in energy (-4.580/-4,699 eV) and both mainly composed of formal d_{z^2}-orbitals at the titanium centers and only small contributions from orthogonal *p*-orbitals at the nitrogen atoms. In addition, the spin density diagram only shows spin localization at the Ti centers in the d_{z^2}-orbitals (Figure 5a, right) which explains the lack of significant Fermi contact interactions with ¹⁴N. At 100K in a glassy matrix, an unusual coupling pattern is present (Figure 5a, left). By spectral simulation, this could be attributed to a pair of dipolar coupled Ti radicals each possessing nearly axial g tensors ($\mathbf{g}_1 = [1.977, 1.978, 1.991]$, $g_{1,\mathrm{iso}} = 1.982$; $\mathbf{g}_2 = [1.981, 1.993, 1.993]$, $g_{2,\mathrm{iso}} = 1.989$) and a coupling tensor of $\mathbf{D} = [42,\ 21,\ 188]$ MHz, $J = 84$ MHz (with J being

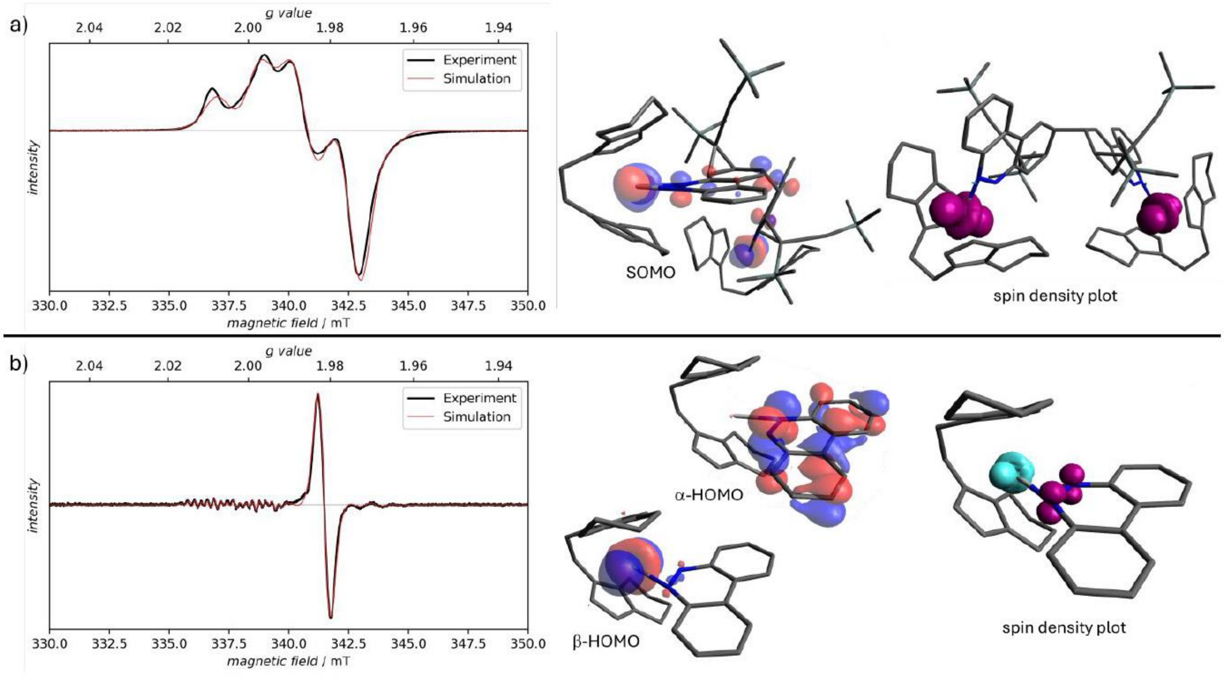
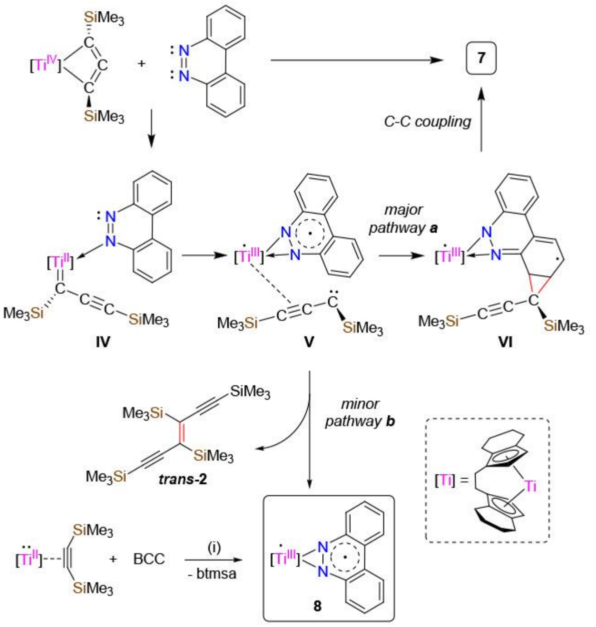


Figure 5. a) Representation of experimental (black) and simulated (red) EPR spectrum of **7** in glassy toluene matrix at 100 K (left), SOMO and spin density plot of **7** (right) calculated on optimized geometry as triplet species; b) Plot of experimental (black) and simulated (red) EPR spectrum of **8** in liquid phase of toluene at 275 K (left), α-HOMO, β-HOMO and spin density plot of **8** (right) calculated on SC-XRD structure as open shell singlet species. Hydrogen atoms are omitted for clarity, level of theory B3LYP-D3/def2-TZVP.

the isotropic exchange interaction according to the coupling Hamiltonian $\hat{H}_{ee} = +\hat{S}_1\mathbf{D}\hat{S}_2$). From calculated and experimental (XRD) structures, the distance between the metal centers is between 10.7 Å (calc.) and 11.1 Å (exp.). Thus, the expected dipolar coupling constant should be ~40 MHz which is very close to the value measured by EPR of 52 MHz. According to the calculations (see above), the two Ti have nearly collinear orbitals which allow for a small overlap and results in the relatively small exchange coupling. Furthermore, the violation of the point-dipole approximation is the likely reason for the slight deviation from axiality and increase of the dipolar coupling constant. Note that the interaction is not visible in the solution spectrum as the anisotropic part is averaged by molecular tumbling while the isotropic coupling is larger than the small spectral separation of the two Ti centers which is estimated as ~35 MHz based on the difference of the isotropic g values. This strong coupling condition leads to a single homogeneously broadened line and loss of otherwise expected hyperfine interaction to magnetic Ti isotopes.

With the above-described formation of the Zr complex **3** in mind, we suggest the following mechanistic sequence for the formation of the Ti complex **7**. First, BCC is likely to coordinate with a free electron pair at the Ti center which leads to Ti-C_{allene} bond cleavage and a formal alkynylcarbene/alkylidene Ti=CR_2 complex **IV**[12] (Scheme 4). The alkynylcarbene resonance form **V** of this species[25] is proposed to be relevant for the formation of **7**. We assume that in the major pathway **a** the alkyne unit remains coordinated at the titanium center, keeping its carbene unit in proximity to a C=C double bond of the BCC. As a result, cyclopropanation occurs at the BCC unit. In contrast to a comparable Zr intermediate during formation of **3**, the M-N distances are likely to be shorter for the Ti complex, which explains the observed divergent activation of BCC. Cyclopropanation leads to electron exchange, dearomatization and a radical center localized in *para* position, which subsequently undergoes C-C coupling, producing **7**. Similar coordination-induced dearomatization/dimerization processes were reported before, e.g., by Fortier and co-workers for a Ti(IV) guanidinate complex upon reaction with pyridine.[26] As an alternative, in minor pathway **b** (Scheme 4), dissociation of the C_3 ligand could furnish ***trans*-2** and a Ti-BCC species. In fact, minor amounts of ***trans*-2** were detected in ^{1}H NMR spectra of reaction solutions (Figure S9). Additionally, broad ^{1}H resonances suggest the presence of either paramagnetic Ti(III) or a dynamic species.

Scheme 4. Possible Mechanisms for the formation of complex 7 and reaction sequence for formation of complex 8: Reaction conditions: (i) benzene, room temperature, 1 h.



To further support this proposed mechanism and shed light on the proposed minor pathway **b**, we have investigated the reactivity of BCC with [*rac*-(ebthi)Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)] as Ti(II) source (Scheme 4, bottom). This transformation avoids the generation of the highly reactive C$_3$ ligand [Me$_3$SiC$_3$SiMe$_3$] in carbene, radical, or ionic form. This reaction occurs at room temperature and within two hours a black solid can be isolated in 65% yield, identified as the mononuclear BCC-coordinated complex **8** by SC-XRD (Figure 6). The ^{1}H NMR spectrum of **8** shows broad signals, likely due to the Cp (δ 3.89, 4.55 ppm) and the BCC protons (δ 11-15 ppm, Figure S50), that are identical to those observed in monitoring of reactions leading to **7** (vide supra). Of note, no resonances could be found in ^{13}C NMR spectra, either due to poor solubility, dynamic behavior, or the presence of paramagnetic species.

The molecular structure of **8** shows the BCC ligand in symmetrical η^2-coordination to the Ti center with bond lengths in the range of Ti-N single bonds (Σr$_{cov}$ 2.07 Å[21], Ti1-N1 2.057(1), Ti1-N2 2.065(1) Å). Electron transfer from the former Ti(II) center to the BCC ligand can be assumed from the coplanar arrangement of the three- and six-membered rings as it was proposed[27] and seen previously, e.g., in decamethyltitanocene(III) bipyridine[28] and acetylpyridine complexes.[29]

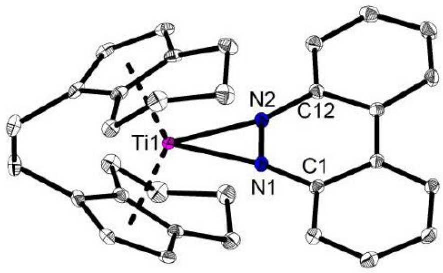


Figure 6. Molecular structure of complex **8**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1-N1 2.0571(13), Ti1-N2 2.0647(13), N1-N2 1.3549(19), N1-C1 1.366(2), N2-C12 1.363(2), N1-Ti1-N2 38.38(5).

In previous work, we have identified Ti(III) triplet species by EPR spectroscopy.[29] In contrast to this, we have not succeeded in directly observing the spin-coupled radical pair of **8** with an expectedly large electron-electron interaction. Instead, EPR spectroscopy suggests the presence of two individual radical centers, not in line with a Ti(III) triplet species (Figure S59). Both signals are well visible at ambient conditions, while at 100 K only the Ti signal ($\mathbf{g} = [1.962,\ 1.983,\ 2.001]$, $g_{\text{iso}} = 1.982$) is left visible due to anisotropic broadening and potentially power saturation of the organic radical. At ambient temperature, the organic radical has an isotropic g-value of $g_{iso} = 2.0032$, whereas the metal-centered radical on Ti has $g_{iso} = 1.9814$. While the Ti-radical is isotropic, with only the expected minority component showing the hyperfine couplings ($A = 24$ MHz) to the two lowly abundant spin-bearing Ti isotopes ^{47}Ti ($I = 5/2$, n.a. 7.3%) and ^{49}Ti ($I = 7/2$, n.a. 5.5%), the organic part is split into a multifold of lines. Spectral simulation with hyperfine couplings to two ^{14}Ns (23.5 and 21.5 MHz, respectively) and three pairs of protons (with 9, 7, and 1.5 MHz, respectively, Figure 5b, left) shows an excellent agreement with the experiment. This shows that the Ti-centered radical has a large localization of the electron spin to the metal atom, while the organic radical features an electron spin density spread over the whole aromatic BCC ligand. The absence of coupling due to electron-electron dipolar interaction at 100 K together with the fact that the absolute EPR signal intensity in samples of **8** is much smaller than those of **7** indicates that dissociation into individual radicals occurs. Nevertheless, the presence of Ti-centered and organic radicals support initial electron transfer from Ti(II) to the BCC ligand. Thus, we assume that the strongly coupled radical pair in **8** is effectively EPR silent. Calculation of the singlet-triplet gap on B3LYP-D3/def2-TZVP level of theory using the SC-XRD data shows that the open-shell singlet state is thermodynamically preferred ($\Delta E_{S\text{-}T}$ = -7.65 kJ mol^{-1}). Analysis of the molecular orbitals shows that the α-HOMO can be best described as bonding and antibonding orbitals located at the BCC fragment, whereas the β-HOMO is mainly composed of the Ti d_{z^2} orbital (Figure 5b, center). The resulting spin density is mainly localized on the metal and the N atoms, leading to a strongly antiferromagnetically coupled Ti(III)/radical anionic BCC system, in agreement with the absence of EPR signals for diamagnetic **8**. Based on these data, we assume that the broad features in the ^{1}H NMR spectra (vide supra) could originate from dynamic flipping/dissociation of the BCC ligand at/from titanium. A more detailed and systematic study of such processes in this and related systems is beyond the scope of this work.

Regarding the mechanism of formation of the dinuclear paramagnetic complex **7**, these control experiments indicate that (i) since compound **8** does not dimerize, the presence of the redox active C_3 fragment[13] is essential for the formation of complex **7**, and (ii) dimerization occurs after cyclopropanation of the coordinated BCC unit.

CONCLUSION

We have presented reactions of the diazenes azobenzene and benzo[*c*]cinnoline with 1-metallacyclobuta-2,3-diene complexes. Depending on the diazene substrate, the metal and the oxidation state of the metallocene precursor, divergent reactivity was observed, ranging from simple η^2-coordination of the diazene, to electron transfer, N-C coupling and dearomatization of the substrate. The reactions of Ti and Zr complexes with geometrically restricted benzo[*c*]cinnoline represent the first examples of redox-activity of 1-metallacyclobuta-2,3-dienes. Furthermore, formation of the unusual dinuclear Ti complex **7** that is proposed to occur via an alkynylcarbene intermediate supports previous findings where these four-membered metallacycles were discussed as masked alkylidene precursors. Future studies will aim at the further exploration of ligand-centered reactivity in these complexes for stoichiometric and catalytic bond formation.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out in an oxygen- and moisture-free argon atmosphere using standard Schlenk and drybox techniques. The solvents were purified with the Grubbs-type column system "Pure Solv MD-5" and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Azobenzene (98%, Sigma-Aldrich), benzo[c]cinnoline (98%, BLDpharm), *rac*-1,2-ethylene-1,1'-bis(η^5-indenyl)zirconium(IV) dichloride ([*rac*-(ebi)$ZrCl_2$]) (LANXESS) were transfer into the glovebox and used as received. Complexes [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)], [*rac*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)], [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] were prepared according to the literature.[30] ^{1}H NMR spectra were recorded on a Bruker 300 and 400 MHz spectrometer and are referenced relative to C_6D_6 at δ 7.16 ppm. ^{1}H NMR data are reported as follow: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). ^{13}C NMR and other 2D NMR spectra were recorded on a Bruker AV400 MHz spectrometer and are referenced to C_6D_6 at δ 128.06 ppm. MS analysis was done using a Finnigan MAT 95-XP instrument (Thero-Electron) in CI$^+$/CI$^-$ mode (isobutene). X-ray diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer. CHN analysis was using a Leco TruSpec elemental analyser.

Synthesis of complex 1 and compound *cis*-2. [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] (0.40 mml, 212 mg, 2 equiv.) and azobenzene (0.20 mmol, 36 mg, 1 equiv.) were dissolved in benzene (10 mL). After heating at 80 °C for 16 h, black precipitates appeared from the brown solution. The solvent was concentrated slowly in vacuum and more precipitated were obtained. The concentrated solution was cannula-filtered to a flask and the left precipitates were washed with pentane to obtain the pure product **1** (87%, 152 mg). The left solution was collected and concentrated, the product ***cis*-2** was separated by flash column chromatography (hexane) from the left concentrated solution. Crystals of complex **1** suitable for SC-XRD analysis were grown from benzene under room temperature.

Data for **1**: ^{1}H NMR (25 °C, benzene-d_6, 400.13 MHz): δ 7.50 (dt, $J_{H,H}$ = 8.3, 1.1 Hz, 4H, 4 x C*H* ebi), 7.21 (dd, $J_{H,H}$ = 3.0, 0.7 Hz, 4H, 4 x C*H* ebi), 7.10 (dq, $J_{H,H}$ = 8.3, 0.9 Hz, 4H, 4 x C*H* ebi), 6.81-6.75 (m, 6H, 6 x C*H* Ph), 6.50-6.41 (m, 8H, 8 x C*H* ebi), 6.08 (d, $J_{H,H}$ = 3.0 Hz, 4H, 4 x C*H* ebi), 5.65-5.62 (m, 4H, 4 x C*H* Ph), 3.20-3.05 (m, 8H, 4 x CH_2 ebi). ^{13}C{^{1}H} NMR (25 °C, benzene-d_6, 100.63 MHz): δ 153.4 (*C* Ph), 131.5 (*C* ebi), 126.6 (*C* ebi), 126.3 (*C*H Ph), 124.9 (*C*H ebi), 123.4 (*C*H Ph), 123.1 (*C*H ebi), 122.9 (*C*H ebi), 120.9 (*C*H ebi), 119.8 (*C* ebi), 119.6 (*C*H Ph), 114.3 (*C*H ebi), 98.2 (*C*H ebi), 27.1 (CH_2 ebi). Elemental analysis calcd (%) for M($C_{52}H_{42}N_2Zr_2$) = 877.37 g mol^{-1}: C 71.19, H 4.83, N 3.19; found: C 70.53, H 4.27, N 3.18. MS-CI$^+$ (*isobutane*): [M$^+$] 876 (4), [(NPh+2H)$^+$] 94 (98). Data for ***cis*-2**: ^{1}H NMR (25 °C, benzene-d_6, 400.1 MHz): δ 0.29 (s, 18H, Me_3Si-C), 0.27 (s, 18H, Me_3Si-C). ^{13}C{^{1}H} NMR (25 °C, benzene-d_6, 100.6 MHz): δ 147.7, 110.0, 107.3, 1.0, 0.4. ^{29}Si-inept NMR (25 °C, benzene-d_6, 79.5 MHz): δ -6.04, -18.83.

Synthesis of complex **3**. Complex [*rac*-(ebi)Zr($Me_3SiC_3SiMe_3$)] (0.10 mmol, 53 mg, 1 equiv.) and benzo[*c*]cinnoline (0.10 mmol, 18 mg, 1 equiv.) were dissolved in toluene (10 mL) at -78 °C and stirring for 0.5 hour, and then slowly warm to 0 °C stirring another 0.5 hour. The color of the solution changed from orange to dark red. The solution was concentrated slowly in vacuum under room temperature and then stored at -30 °C overnight to obtained product **3** (76%, 54 mg) as dark red crystals. Crystals suitable for SC-XRD analysis were grown from toluene at -30 °C. ^{1}H NMR (25 °C, benzene-d_6, 400.13 MHz): δ 7.70 (dt, $J_{H,H}$ = 8.3, 1.1 Hz, 1H, 1 x C*H* ebi), 7.52(m, 1H, 1 x C*H* ebi), 7.19 (m, 1H, 1 x C*H* BCC), 7.08-6.89 (m, 4H, 4 x C*H* ebi), 6.84-6.77 (m, 1H, 1 x C*H* BCC), 6.73 (t, $J_{H,H}$ = 7.5 Hz, 1H, 1 x C*H* ebi), 6.60-6.55 (d, $J_{H,H}$ = 8.0 Hz, 1H, 1 x C*H* ebi), 6.53-6.44 (m, 2H, 2 x C*H* BCC), 6.38 (d, $J_{H,H}$ = 3.3 Hz, 1H, 1 x C*H* ebi), 6.35 (dd, $J_{H,H}$ = 3.2, 0.7 Hz, 1H, 1 x C*H* ebi), 5.93-5.84 (m, 1H, 1 x C*H* BCC), 5.70-5.63 (m, 1H, 1 x C*H* BCC), 5.63 (d, $J_{H,H}$ = 3.1 Hz, 1H, 1 x C*H* ebi), 5.57-5.51 (m, 1H, 1 x C*H* BCC), 5.33 (m, 1H, 1 x C*H* BCC), 4.84 (m, 1H, 1 x C*H* BCC), 3.49-3.31 (m, 2H, 1 x CH_2 ebi), 3.21-3.07 (m, 2H, 1 x CH_2 ebi), 0.39 (s, 9H, 3 x CH_3 $SiMe_3$), 0.26 (s, 9H, 3 x CH_3 $SiMe_3$). ^{13}C{^{1}H} NMR (25 °C, benzene-d6, 100.63 MHz): δ 194.5 (Zr-*C*), 141.3, 136.8, 132.3, 128.7, 128.0, 127.4, 127.0, 126.0, 125.5, 124.7, 124.7, 124.6, 124.1, 124.1, 123.7, 123.4, 122.8, 122.8, 122.6, 120.2, 118.9, 118.0, 116.5, 112.7, 102.4, 101.4, 100.3, 94.1, 78., 47.1 (BCC), 32.1 (ebi), 28.6 (ebi), 2.9 ($SiMe_3$), 2.1 ($SiMe_3$). Elemental analysis calcd (%) for $M(C_{32}H_{26}N_2Zr)$ = 710.2 g mol-1: C 69.34, H 5.96, N 3.94; found: C 69.10, H 5.79, N 3.81. MS-CI+ (*isobutane*): [M-H+] 709 (100), [(*rac*-ebthi+3H)+] 259 (12).

Synthesis of complex *rac*-4 and *trans*-4. Complex [*rac*-(ebi)$ZrCl_2$] (3 mmol, 1255.4 mg, 1 equiv.) and Li (12 mmol, 84 mg, 4 equiv.) were mixed and dissolved in benzene (40 mL) under room temperature. Then the bis(trimethylsilyl)acetylene (3 mmol, 511.2 mg, 1 equiv.) was added into the flask. The reaction mixture was stirring under 60 °C for 8 days. Monitor by ^{1}H NMR, when the [*rac*-(ebi)$ZrCl_2$] was consumed, the brown solution was cannula-filtered. The benzene solution was concentrated and stored at room temperature to obtain complex ***rac*-4** (89%, 1383 mg) as a golden yellow crystal. Crystals suitable for SC-XRD analysis were grown from benzene under room temperature. Note: when use toluene as solvent instead of benzene, a green solution can be obtained, after cannula-filter and concentrated, a mixture of golden yellow crystals for complex ***rac*-4** and green crystals for complex ***trans*-4** were obtained under -78 °C.

Data for ***rac*-4**: ^{1}H NMR (25 °C, benzene-d6, 400.13 MHz): δ 7.93 (d, $J_{H,H}$ = 3.2 Hz, 2H, 2 x CH ebi), 7.77-7.70 (m, 2H, 2 x CH ebi), 6.81-6.69 (m, 4H, 4 x CH ebi), 6.52-6.43 (m, 2H, 2 x CH ebi), 5.01 (d, $J_{H,H}$ = 3.4 Hz, 2H, 2 x CH ebi), 2.46-2.23 (m, 4H, 2 x CH_2 ebi), -0.09 (s, 18H, 6 x CH_3, $SiMe_3$). $^{13}C\{^1H\}$ NMR (25 °C, benzene-d6, 100.63 MHz): δ 259.8 (C-$SiMe_3$), 128.7 (CH ebi), 126.4 (C ebi), 125.5, 122.2, 118.4, 116.9 (4 x CH ebi), 112.9 (C ebi), 99.6 (CH ebi), 26.1 (CH_2 ebi), 2.1 (CH_3 $SiMe_3$), 0.0 (free btmsa). Elemental analysis calcd (%) for $M(C_{28}H_{34}Si_2Zr)$ = 517.97 g mol-1: C 64.93, H 6.62; found: C 63.33, H 6.46. MS-CI+ (isobutane): [(*rac*-ebthi+3H)+] 259 (100), [$Me_3SiC_2SiMe_3$] 170 (13).

Data for ***trans*-4**: ^{1}H NMR (25 °C, benzene-d6, 400.13 MHz): δ7.80-7.76 (m, 2H, 2 x CH ebi), 7.55 (dd, $J_{H,H}$ = 3.3, 0.7 Hz,2H, 2 x CH ebi), 6.85-6.70 (m, 6H, 4 x CH ebi), 5.12 (d, $J_{H,H}$ = 3.3 Hz, 2H, 2 x CH ebi), 2.79-2.32 (m, 4H, 2 x CH2 ebi), 0.15 (s, 9H, 3 x CH_3, $SiMe_3$), -0.30 (s, 9H, 3 x CH3, $SiMe_3$). $^{13}C\{^1H\}$ NMR (25 °C, benzene-d6, 100.63 MHz): δ 262.4 (C-$SiMe_3$), 259.3 (C-$SiMe_3$), 128.9 (CH ebi), 127.3 (C ebi), 125.4, 123.0, 120.1, 119.0 (4 x CH ebi), 113.6 (C ebi), 96.3 (CH ebi), 27.1 (CH_2 ebi), 3.0 (CH_3 $SiMe_3$), 1.6 (CH_3 $SiMe_3$).

Synthesis of complex 5. ***rac*-4** (0.20 mmol, 103.6 mg, 1 equiv.) azobenzene (0.20 mmol, 36.5 mg, 1 equiv.) were dissolved in benzene (5 mL) and stirring for 10 min, then the solvent was removed by vacuum, a brown solid was obtained. Then the solid was washed by hexane for three times and dried under vacuum, give complex **5** as a brown solid (68%, 68 mg). Crystal suitable for SC-XRD analysis were grown from benzene at room temperature. ^{1}H NMR (25 °C, benzene-d_6, 400.13 MHz): δ 7.28 (m, 2H, 2 x C*H* Ph), 7.20-7.11 (m, 2H, 2 x C*H* Ph), 7.05-6.97 (m, 4H, C*H* ebi), 6.88-6.78 (m, 4H, 2 x C*H* ebi, 2 x C*H* Ph), 6.67-6.60 (m, 2H, 2 x C*H* ebi), 6.48-6.36 (m, 4H, 4 x C*H* Ph), 6.23 (m, 2H, 2 x C*H* ebi), 6.00 (d, $J_{H,H}$ = 3.5, 2H, 2 x C*H* ebi), 3.12-2.82 (m, 4H, 2 x CH_2 ebi). $^{13}C\{^1H\}$ NMR (25 °C, benzene-d_6, 100.63 MHz): δ 157.9 (*C* Ph), 128.8 (CH Ph), 128.4 (CH Ph), 126.5 (CH ebi), 126.3 (CH ebi), 125.4 (*C* ebi), 124.0 (*C* ebi), 122.9 (CH ebi), 119.1 (CH Ph), 118.0 (CH ebi), 117.5 (*C* ebi), 116.7 (CH Ph), 111.9 (CH ebi), 111.4 (CH Ph), 107.3 (CH ebi), 27.3 (CH_2 ebi). Elemental analysis calcd (%) for $M(C_{32}H_{26}N_2Zr)$ = 529.80 g mol-1: C 72.55, H 4.95, N 5.29; found: C 71.42, H 4.79, N 5.18. MS-CI+ (*isobutane*): [(NPh+3H)+] 94 (51), [(*rac*-ebthi+3H)+] 259 (100), [(M+2H)+] 530 (2).

Synthesis of complex 6. [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)] (0.20 mmol, 98.9 mg, 2 equiv.) and azobenzene (0.10 mmol, 18.2 mg, 1 equiv.) were dissolved in benzene (3.0 mL) in a Schlenk flask. After heating at 80 °C for 3 days, the color of the mixture changed from red to brown, remove solvent by vacuum, a brown solid **6** was obtained (59.5 mg, 88.0 % isolated yield; 33% nmr yield, internal standard method). ^{1}H NMR (25 °C, [D6]benzene, 400.13 MHz): δ = 7.51 (t, $J_{H,H}$ = 7.5 Hz, 1H, 1 x C*H* Ph), 7.38 (m, 1H, 1 x C*H* Ph), 7.30 (m, 1H, 1 x C*H* Ph), 7.13 (m, 2H, 2 x C*H* Ph), 6.91 (m, 2H, 2 x C*H* Ph), 6.84 (m, 1H, 1 x C*H* Ph), 6.62 (d, $J_{H,H}$ = 3.0 Hz, 1H, 1 x C*H* ebthi), 6.53-6.42 (m, 2H, 2 x C*H* Ph), 6.30 (d, $J_{H,H}$ = 2.9 Hz, 1H, 1 x C*H* ebthi), 5.41 (d, $J_{H,H}$ = 3.0 Hz, 1H, 1 x C*H* ebthi), 5.30 (d, $J_{H,H}$ = 3.1 Hz, 1H, 1 x C*H* ebthi), 3.00-1.10 (m, 20H, 10 x CH_2, ebthi), 0.24 (s, 9H, 3 x CH_3, $SiMe_3$), 0.05 (s, 9H, 3 x CH_3, $SiMe_3$). $^{13}C\{^1H\}$ NMR (25 °C, [D6]benzene, 75.49 MHz): δ = 159.8 (*C* Ph), 158.1 (*C* Ph), 136.4, 133.1, 129.5 (3 x *C* ebthi), 129.3 (*C*-SiMe3), 129.1, 128.8 (2 x CH Ph), 127.6, 122.6, 121.7 (3 x *C* ebthi), 121.0, 120.6, 120.0 (3 x CH Ph), 118.5, 117.9 (2 x C ebthi), 117.5, 112.0, 110.4 (3 x CH Ph), 109.0 (C=*C*=C), 108.8, 103.8 (2 x *C* ebthi), 87.0 (*C*-$SiMe_3$), 33.8, 31.3, 29.4, 28.6, 25.9, 25.0, 25.0, 24.6, 24.3, 23.0 (10 x CH_2 ebthi), 0.7, -2.9 (9 x CH_3 $SiMe_3$). ^{29}Si-inept NMR (25 °C, [D6]benzene, 79.49 MHz): δ = 4.56, -20.78. Elemental analysis calcd (%) for $M(C_{41}H_{52}N_2Si_2Ti)$ = 676.92 g mol-1: C 72.68, H 7.68, N 4.14; found: C 71.38, H 7.51, N 4.08. MS-CI+ (isobutane): [M+] 676 (100), [M-$SiMe_3$+] 605 (46), [(M-NPh)+] 512 (31).

Synthesis of complex 7. [*rac*-(ebthi)Ti($Me_3SiC_3SiMe_3$)] (0.14 mmol, 69.6 mg, 1 equiv.) and benzo[c]cinnoline (0.14 mmol, 25.4 mg, 1 equiv) were dissolved in benzene (10 mL) and stirring for 24 h under 60 °C, the color of the solution changed from purple to red. After the reaction, the solvent was removed by vacuum, use hot hexane wash the solid and filter. Concentrated the hexane solution and the orange crystal 1d grow under room temperature (82.0 mg, 87%). Crystal suitable for SC-XRD analysis were grown from hexane at room temperature. Elemental analysis calcd (%) for $M(C_{82}H_{100}N_4Si_4Ti_2)$ = 1349.8 g mol-1: C 72.97, H 7.47, N 4.15; found: C 72.42, H 7.39, N 4.08. MS-CI+ (*isobutane*): [(benzo[c]cinnoline+H)+] 181 (100), [$Me_3SiCH_2C_2SiMe_3$] 182 (13), [monomer] 675 (4).

Synthesis of complex 8. Complex [*rac*-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$)] (0.10 mmol, 48.3 mg, 1 equiv) and benzo[c]cinnoline (0.1 mmol, 18.0 mg, 1 equiv) were dissolved in benzene (10 mL) and stirring for 2 h under room temperature, the color of the solution changed from brown to dark blue. Then the solvent was removed by vacuum, use toluene wash the solid and filter several times. Concentrated the toluene solvent and black crystal 1e grow under room temperature (32.0 mg, 65%). Crystals suitable for SC-XRD analysis were grown from toluene at room temperature by slow evaporate the toluene, the Schlenk flask need to be placed vertically but not diagonally while evaporate the toluene. ^{1}H NMR (25 °C, benzene-d_6, 400.13 MHz): δ 11-15 (v br, 8 H, C*H*BCC), 4.55 (br s, 2H, C*H* ebthi), 3.89 (br s, 2H, C*H* ebthi), 0-3 ppm (br m, CH_2 ebthi). Elemental analysis calcd (%) for M($C_{32}H_{32}N_2Ti$) = 492.49 g mol^{-1}: C 78.04, H 6.55, N 5.69; found: C 78.65, H 6.64, N 5.48. MS-CI$^+$ (*isobutane*): [M] 492 (100), [(M+H)$^+$] 493 (39), [(M+2H)$^+$] 494 (14).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org.

Experimental details, NMR data (^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC) and crystallographic data for all new compounds, computational details (PDF)

Structures of all the computationally modeled structures (XYZ)

Accession Codes

CCDC 2346622-2346628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.cced.cam.sc.uk/data_request/cif, or by emailing data_request@cced.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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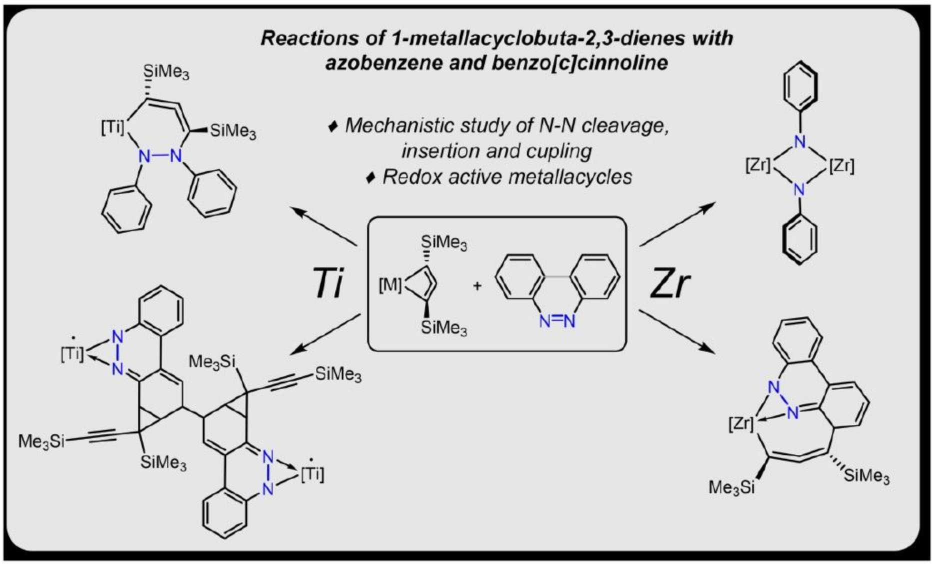

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5 Curriculum Vitae

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Publications

1. S. Li, M. Schröder, X. Shi, A. Spannenberg, J. Fischer, B. Corzilius,* F. Reiß,* T. Beweries,* *manuscript submited*.
2. S Li, M. Schröder, A. Prudlik, X. Shi, A. Spannenberg, J. Rabeah, R. Francke,* B. Corzilius,* F. Reiß,* T. Beweries,* *Chem. Eur. J.* **2024**, e202400708.
3. X. Shi,[†] S. Li,[†] A. Spannenberg, F. Reiß*, T. Beweries,* *Inorg. Chem. Front.* **2023**, *10*, 3584-3594.
4. X. Shi, S. Li, M. Reiß, A. Spannenberg, T. Holtricter-Rößmann, F. Reiß,* T. Beweries,* *Chem. Sci.* **2021**, *12*, 16074-16084.

Conferences

1. 18th Koordinationschemie-Terffen, oral report, 02.2024, Innsbruck, Austria.
2. Evaluation of Leibniz-Institut for Catalysis, poster, 01.2023, Rostock, Germany.
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4. Anglo-German Inorganic Chemistry Conference, poster, 09.2021, Online.