Information

Metallocene-made mad metallacycles in synthesis and catalysis*

U. Rosenthal

Leibniz Institute for Catalysis at the University of Rostock (LIKAT),
29a Albert-Einstein-Str., 18059 Rostock, Germany.
*Fax: +49 (381 12) 815 1176. E-mail: uwe.rosenthal@catalysis.de***

Metallacycles of transition metals are generally of great interest because of their multifaceted structural chemistry and they are often discussed as key intermediates in multiple catalytic processes, whereupon recent studies are dealing with the participation of metallacycles in polymerization as well as oligomerization reactions. Synthesis and characterization of the titanocene bis(trimethylsilyl)acetylene complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ paved the way towards the discovery of three-membered metallacyclopropenes of Group 4 metals (titanium, zirconium, and, later, hafnium) having their own history which is strongly connected with the names of M. E. Vol´pin and his co-workers. Starting from these compounds the very unusual ring-strained "all-C"-five-membered metallacyclocumulenes, metallacyclopentynes, and metallacycloallenes of Group 4 metals were obtained and characterized having all their roots in Vol´pin´s chemistry. This mini review gives an overview of these unusual molecules as well as some more common molecules like metallacyclopentanes, metallacyclopentenes, and metallacyclopentadienes. Very recently instead of these "all-C"-metallacycles the analogous heteroring systems (with N, S, O atoms instead of C) as well as the smaller four-membered metallacycles became the focus of our interest.

Key words: three-, four-, and five-membered metallacycles, Group 4 metals, strained "all-C" and heteroring systems, small four-membered metallacycles.

There are long standing interests in synthetic chemistry to make compounds that have not the conventional molecular structures.[1] This is the case for highly strained and unsaturated cyclic molecules containing structural units of alkynes (—C≡C—), allenes (—RC=C=CR—), and cumulenes (such as —RC=C=C=CR—) in the ring which are linear according to the fundamental rules of orbital symmetry. If such bonds are incorporated into small carbocyclic ring systems, these unsaturated structural motifs significantly deform their geometry and cause enormous ring strain. Incorporating metal centers into the ring unit can reduce strain very effectively and realize unusual structures.[2] Using well suited metals in the ring, synthetic

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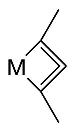
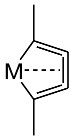
* Dedicated to the memory of Academician M. E. Vol´pin.

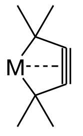
** Leibniz-Institut für Katalyse e.V. an der Universität Rostock (LIKAT), 29a Albert-Einstein-Straße, 18059 Rostock, Deutschland.

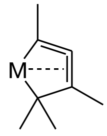
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2577—2582, November, 2014.

chemists not only succeeded in preparing usual molecules like metallacyclopentanes, metallacyclopentenes, and metallacyclopentadienes but also more exotic and more reactive hydrocarbon structures. Starting from "all-C"-metallacycles like three-membered metallacyclopropenes (complexes of alkynes RC≡CR, *e.g.*, $Cp_2M(\eta^2\text{-}Me_3Si\text{-}C_2SiMe_3))$,[3] the very unusual ring-strained "all-C"-metallacyles like **1M** (four-membered metallacycloallenes), **2M** (five-membered metallacyclocumulenes; butadiyne RC≡CC≡CR complexes), **3M** (five-membered metallacyclopentynes; butatriene $H_2C=C=C=CH_2$ complexes) and **4M** (five-membered metallacycloallenes; buteneyne $H_2C=CH-C\equiv CR$ complexes) were obtained and characterized.[4] Very recently, instead of these "all-C"-metallacyles, the analogous heteroring systems became the focus of our interest.[5—7]


1M

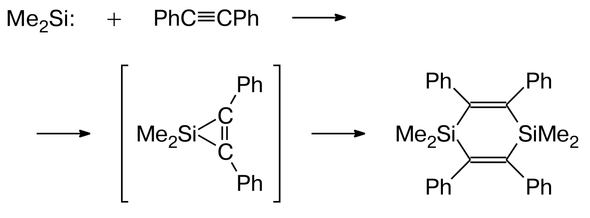

2M


3M


4M

Often, the success in synthetic organometallic chemistry depends on well suited starting materials. In the here considered case, the chemistry of the three-membered metallacyclopropenes of titanium, zirconium as well as later of hafnium has its own history and is strongly connected with the names of M. E. Vol´pin and his co-workers. In 1961, he described the synthesis of the first silacyclopropene by the reaction of silylene [Me_2Si:] with diphenylacetylene PhC≡CPh (Scheme 1).[8] Later, X-ray investigations[9] of this compound showed a six-membered but not the assumed three-membered ring for the molecular structure.

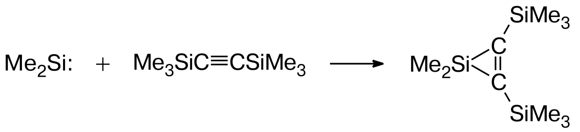
Scheme 1



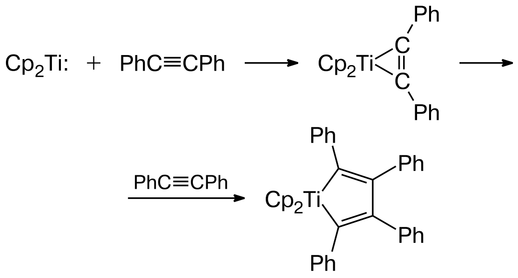
By changing the substituents and using the Me_3Si group instead of the phenyl substituent at the alkyne, D. Seyferth and co-workers realized the first silacyclopropene in 1976 (Scheme 2).[10]

The same alkyne, $Me_3SiC\equiv CSiMe_3$, we used for the Ni^0 alkyne complexes such as $(Ph_3P)_2Ni(\eta^2\text{-}Me_3SiC_2SiMe_3)$ in a series of Ni^0 compounds $L_2Ni(\eta^2\text{-}RC_2R)$ to study the influence of the alkyne substituents R and different ligands L on the alkyne complexation by spectroscopic methods (IR and Raman spectroscopy, ^{13}C NMR spectroscopy, *etc.*) and the characterization of the molecular structure of the compounds by X-ray investigations.[11] Having in mind to evaluate the influence of the metals and to switch from the late to the early transition metals, the author moved to Nesmeyanov Institute of Organoelement Compounds of the Academy of Science of USSR (at present, INEOS RAS) in Moscow where such complexes of titanocene with PhC≡CPh lacking other ligands, *viz.*, $Cp_2Ti(\eta^2\text{-}PhC_2Ph)$, were described (Scheme 3) but without molecular structure. Additionally, this compound had the tendency to form titanacyclopentadienes by oxidative coupling.[12]

Scheme 2

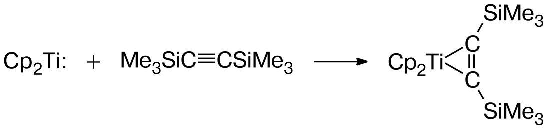


Scheme 3



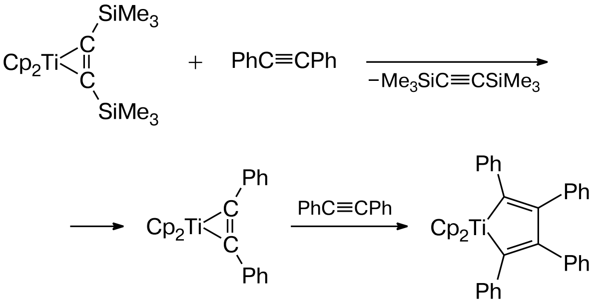
When the author first met M. E. Vol´pin in 1988, he brought more than twenty different alkynes RC≡CR to prepare the titanocene complexes $Cp_2Ti(\eta^2\text{-}RC_2R)$ and to continue the studies on the influence of alkyne substituents R on the synthesis of these compounds. After the above mentioned experience with silicon, Vol´pin with big intuition selected directly only $Me_3SiC\equiv CSiMe_3$ for the following very important investigations which were conducted in the laboratory of V. B. Shur together with V. V. Burlakov (Scheme 4).

Scheme 4



The obtained compound $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^3$ is extremely soluble in common solvents and it took a long time of 15 years to find the molecular structure for this compound.[3] The most surprising fact in the reactivity of this compound is its tendency to dissociate producing alkyne $Me_3SiC{\equiv}CSiMe_3$ (mostly without any coupling) thus giving the complex the chance to act as a source for the very reactive unstable $[Cp_2Ti]$ species under very mild conditions. This was first found in the reaction of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with $PhC{\equiv}CPh$ (Scheme 5).[3]

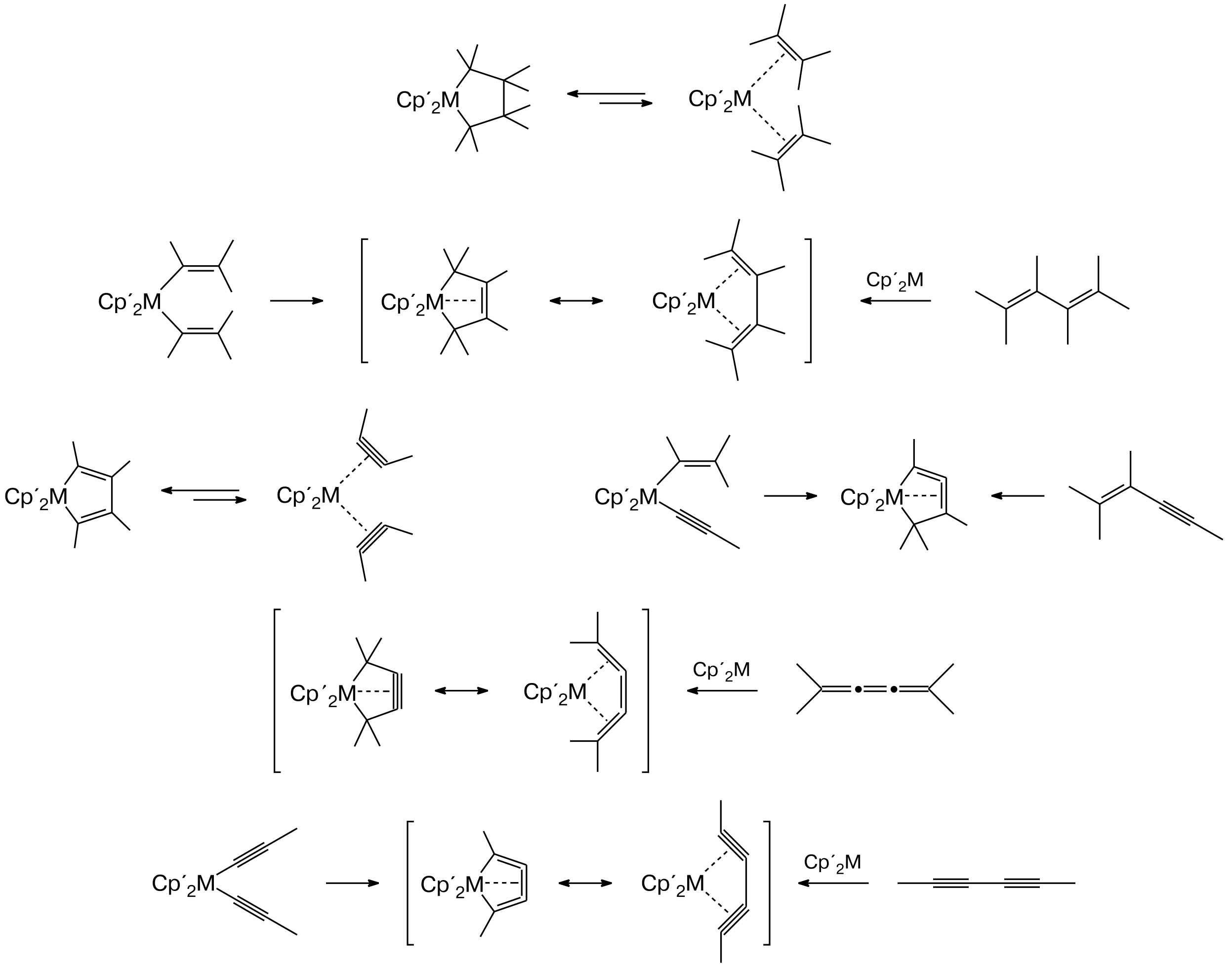
Scheme 5



This reaction opened the door for many stoichiometric and catalytic reactions with a lot of substrates, which were summarized in several book contributions and reviews.[3] The reactivity of complexes $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp´ is a substituted Cp) strongly depends on the used substituted Cp´ ligands and metals (Ti, Zr, and Hf). One special aspect is the formation of the above mentioned and hitherto unknown unusual metallacycles[5—7] (Scheme 6).

Examples given on Scheme 6 include syntheses of metallacyclocumulenes, metallacycloallenes, and metallacycloalkynes, *i.e.*, the compounds found and intensively investigated by the groups of G. Erker and N. Suzuki.[5] In all cases, the early transition metal atom plays a significant role in the stabilization of the small cyclic structural elements. These complexes were obtained either directly by complexation of unsaturated compounds like butadiynes (RC≡C—C≡CR), but-ene-ynes (RC≡C—CH=CR$_2$), and trienes (R$_2$C=C=C=CR$_2$) or *in situ* after the reductive coupling of two alkynyl (RC≡C—), alkynyl (RC≡C—) with alkenyl (—CH=CR$_2$) or two alkenyl

Scheme 6

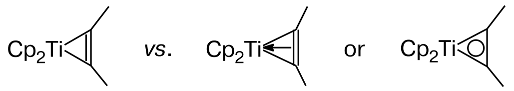


Cp´ is the substituted Cp.

(—CH=CR$_2$) groups followed by complexation of the formed unsaturated compounds.

The less strained five-membered metallacycles such as metallacyclopentadienes, -pentenes, and -pentanes often show a rich chemistry and by oxidative or hydrolytic workup give rise to metal-free analogs. In addition, in catalytic applications such as cyclizations or oligomerizations, these compounds play an important role either as the key intermediates or as catalyst complexes.[13]

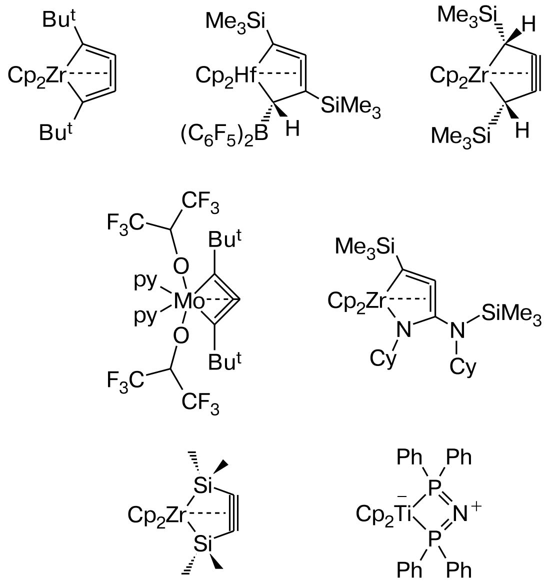
There is some controversy over the bonding characterization and whether such compounds could be described as the π complexes or metallacycles with an aromatic character, or the in-between of both.[14] Computational techniques have also been used to explore these questions and to predict the reactivity of such compounds. This interesting question was originally raised by Vol´pin and co-workers who discussed the aromaticity in three-membered metallacyclopropenes and how these interactions could stabilize such unusual structures.[15]



A similar question if the unusual metallacycles like metallacyclocumulenes, metallacycloallenes, and metallacycloalkynes should be considered as the π complexes or as metallacycles with an aromatic character was discussed as in the case of the three-membered metallacyclopropenes.[12,15]

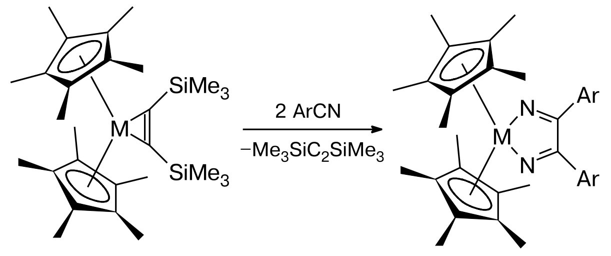
Switching from exotic three- and five-membered "all-C"-metallacycles to heterometallacycles leads to two different modes of stabilization coming from the addition of the heteroatoms or metal centers to the strained cyclic structures. The heteroatoms or metals mostly have longer bond distances to the attached C atoms compared to the equivalent C—C bond, and some metal centers can interact with the π electrons of the unsaturated metallacycle moieties. Both effects can reduce the ring strain and lead to the stable, isolable organometallic compounds. Below some examples of exotic four- and five-membered metallacycles[5—7] are given: zirconacyclocumulene (1-zirconacyclo-2,3,4-triene), hafnacycloallene (1-hafnacyclopenta-2,3-diene), zirconacycloalkyne (1-zirconacyclopent-3-yne), 1-molybdenacyclobuta-2,3-diene, 1-zircona-2-azacycloallene, 1-zircona-2,5-disilacyclopent-3-yne, and hetero-1-titanacycloallene.

In addition to the interest in their structural features, some of these exotic molecules can also be regarded as the model complexes for stoichiometric and catalytic conversions mediated by transition metal centers. A combination of metals and heteroatoms has allowed the isolation of even more strained azacycloallenes, disilacyclopent-3-ynes, and a series of different hetero-1-metallacyclobuta-2,3-dienes.[5—7]



Our recent investigations are concentrated to find other unusual five-membered heterometallacycles. We found the formation of unusual 1-metalla-2,5-diaza-1,4-dienes by C—C-coupling of aryl nitriles (Scheme 7). It is worth to mention that these ring strained heterometallacycles differ from the well-known 1,4-diazabuta-1,4-diene complexes (1-metalla-2,5-diazacyclopent-3-enes).[7f]

Scheme 7

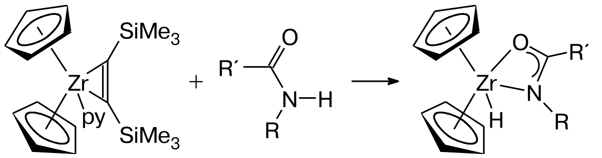


M = Ti, Zr

The other recent question was the existence of four-membered metallacycloallenes (1-metallacyclobuta-2,3-dienes) of the early transition metals. Such highly strained structures as "all-C"-compounds were found to be rather difficult to access for Ti, Zr, and Hf. Nevertheless, according to the theoretical calculations, the incorporation of heteroatoms into metallacycles should stabilize such structures. In a cooperation with L. L. Schafer, we very recently found zirconocene hydrido amidate complexes by formal oxidative addition of the amide N—H bonds to the reduced zirconocene fragments by using Cp$_2$Zr(py)(η^2-Me$_3$SiC$_2$SiMe$_3$) as the starting material (Scheme 8).[7g] Insertion reactions of these compounds with alkenes showed a different behavior than the Schwartz´s reagent by forming branched insertion products.

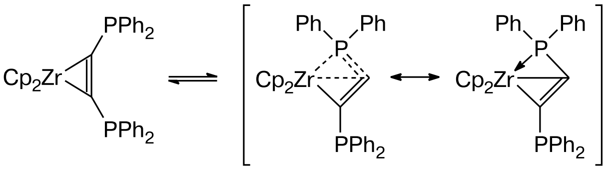
We tried to obtain other four-membered heterometallacycles of this type by using hetero-disubstituted alkynes

Scheme 8



XC≡CX (X = S, B, P, *etc.*). The idea was to initiate a coordination of the heteroatoms X in addition to the triple bond and to access the four-membered heterometallacycles. During these investigations, an interesting result was the coordination of bis(diphenylphosphanyl)acetylene $Ph_2PC{\equiv}CPPh_2$ (Scheme 9) giving some hints for such resonance structures of four-membered highly strained structures in a flip-flop coordination.[7h]

Scheme 9



The driving force in synthesizing all these compounds was to push the boundaries of conventional molecular structures. Chemists have always been interested to make molecules that violates the norm and so exotic, therefore, more unstable hydrocarbon structures have been created. For example, alkynes (RC≡CR), allenes ($R_2C{=}C{=}CR_2$), and cumulenes (such as $R_2C{=}C{=}C{=}CR_2$) are linear and the incorporation of these unsaturated structural motifs into small carbocyclic ring systems significantly deforms their geometry and causes enormous ring strain. However, incorporating metals and/or heteroatoms into such cyclic units reduces this ring strain. Computational techniques have been used to explore these metallacycles and to predict the viability of such other compounds. These theoretical considerations as well as the "serendipity" of daily research will create in future other such highly interesting organometallics.

Additionally, at the end of this historical review it is worth to mention as an example for the way from basic research to applications that the three-membered metallacyclopropenes react with ethylene to give saturated metallacyclopentanes, which are very important for an industrial application. Such saturated metallacyclic compounds are important as model compounds for the basis of the homogeneously catalyzed selective oligomerization of ethylene resulting in linear *n*-α-olefins. Using these results, we were successful in developing a mononuclear chromium-based homogeneous 1-hexene-selective catalytic system[16] as well as to elaborate a new dinuclear concept for the tetramerisation of ethylene to 1-octene.[17]

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The herein described chemistry started in 1988, when Academician Prof. M. E. Vol´pin was the host for the author as scientific guest in INEOS (Moscow) and gave the most important hints to start these investigations for the following 25 years. Up to now, this spirit is alive as a cooperation with the group of Prof. V. B. Shur together with Dr. Chem. Sci. V. V. Burlakov as well as independently in the LIKAT (Rostock). This chemistry gave many very interesting and unexpected results, which are summarized in this mini review.

First and foremost I am deeply indebted to Academician Prof. Vol´pin for making me a part of his group and providing me with this interesting research project.

My sincere appreciation for the continuous cooperation with Prof. V. B. Shur and Dr. Chem. Sci. V. V. Burlakov.

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Received July 15, 2014;
in revised form September 9, 2014