Unusual Metallacycles

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Discovering Chemical Terra Incognita: Unusual Metallacycles and Their Reactions**

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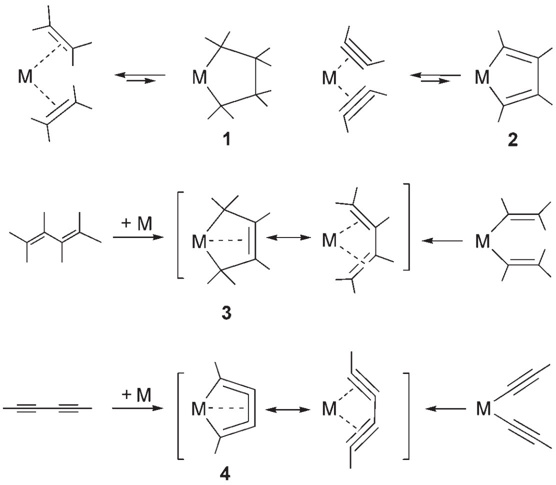
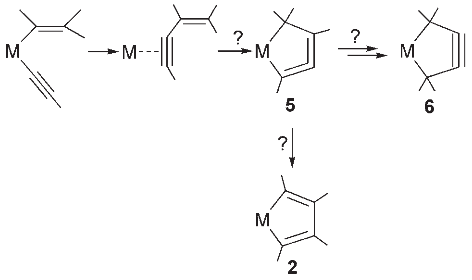
cyclocumulenes · cyclopentynes · hafnium · metallacycles · zirconium

Saturated metallacycles of transition metals are now an important class of organometallic compounds. An current example are metallacyclic compounds formed by oxidative coupling of ethylene, $H_2C{=}CH_2$, via metallacyclopentanes **1** (Scheme 1), leading to the highly selective tri- or tetramerization of ethylene.[1] Similarly, the unsaturated 1-metallacyclopenta-2,4-dienes **2** (4 valences)[2] are formed by oxidative coupling of two alkynes $RC{\equiv}CR$. With certain diolefins and diynes, other unsaturated metallacycles of the early transition metals have been prepared and systematically investigated, which are formed either by coordination of unsaturated molecules or by coupling of anionic ligands.[3] The 1-metallacyclopent-3-enes **3** (6 valences) are obtained by complexation of neutral 1,3-butadienes $RHC{=}CH{-}CH{=}CHR$ or by coupling of two anionic σ vinyl groups starting from $[Cp_2M(CH{=}CHR)_2]$. This classical organometallic chemistry was firstly described by Erker et al. and Nakamura et al.[4a,b] Further species are the unusual 1-metallacyclopenta-2,3,4-trienes **4** (2 valences) formed either by complexation of 1,3-butadiynes $RC{\equiv}C{-}C{\equiv}CR$ or coupling of two anionic σ acetylides starting from $[Cp_2M(C{\equiv}CR)_2]$.[3]



Scheme 1. Formation of symmetrically substituted five-membered metallacycles.

Mixed coupling of anionic σ-acetylides and σ vinyl groups was discussed in a review.[3a] Starting from $[Cp_2M(CH{=}CH_2)(C{\equiv}CH)]$, complexes with the but-1-en-3-yne ligand, $H_2C{=}CH{-}C{\equiv}CH$, formed only simple η^2-π alkyne complexes with titanocene, as found by Mach et al.[4c] In contrast, for the larger zirconocene, η^4-π,π complexation of both unsaturated groups (similar to the butadienes and butadiynes, Scheme 1) and formation of unsymmetrical 1-zirconacyclopenta-2,3-dienes **5** was predicted (Scheme 2).[3a] In addition, the question was raised as to whether cyclopenta-2,3-dienes **5** are stable or could isomerize either to cyclopenta-2,4-dienes **2**[3a] or cyclopent-3-ynes **6**.[5]



Scheme 2. Proposed formation and isomerization of 1-metallacyclopenta-2,3-dienes.

With regard to 1-metallacyclopent-3-ynes **6** (4 valences, Scheme 3), Suzuki and co-workers accomplished an outstanding pioneering work.[5a,b] They started with substituted cyclopent-3-ynes **5**, which were obtained by reactions of zirconocenes with butatrienes $RHC{=}C{=}C{=}CHR$.[5a] Later, the synthesis of unsubstituted 1-metallacyclopent-3-ynes **6** was reported using $H_2C{=}C{=}C{=}CH_2$ generated in situ.[5b]

Very recently, two reports were published, by Erker et al.[6] and Suzuki et al.,[7] on the synthesis of the predicted cyclopenta-2,3-diene complexes **5**,[5a] thus closing the gap

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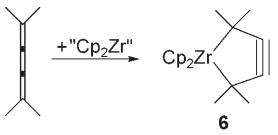
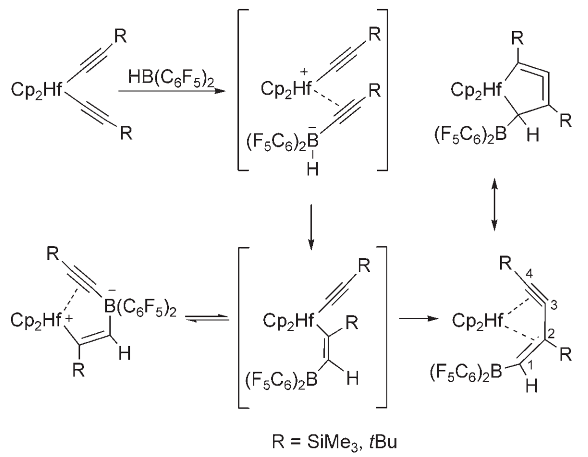


Scheme 3. Preparation of 1-metallacyclopent-3-ynes.

between cyclopent-3-ene complexes **3** and cyclopenta-2,3,4-triene complexes **4**.

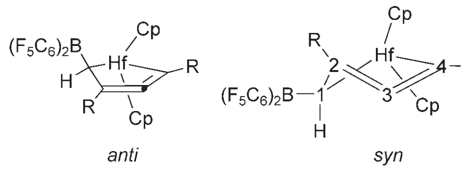
In the first publication,[6] reactions of the complexes $[Cp_2Hf(C\equiv CR)_2]$ (R = $SiMe_3$ and *t*Bu) with $HB(C_6F_5)_2$ are described that form a hafnacycle of the predicted type **5**. The proposed reaction sequence consists of an alkynyl abstraction, 1,1-hydroboration, and C–Hf σ bond formation to give a reactive intermediate with σ acetylide and σ alkenyl groups. This complex undergoes reductive coupling to yield the product (Scheme 4).



Scheme 4. Formation of 1-hafnacyclopenta-2,3-dienes.

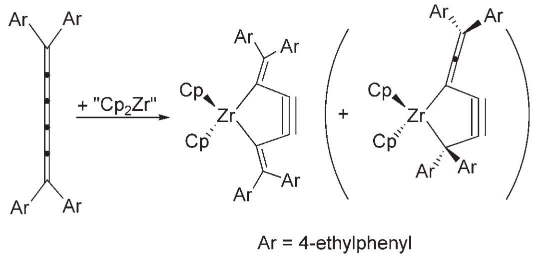
The structure of the product having R = $SiMe_3$ features a five-membered metallacycle with all four carbon atoms in bonding distance to hafnium. The C3–C4 bond is short (1.276(4) Å), the C2–C3 bond is longer (1.356(4) Å), and the C1–C2 bond is in the C–C σ single-bond range (1.490(4) Å). Carbon atom C1 has typical bond angles for a saturated carbon atom in a five-membered ring. The ring system is markedly bent at carbon atom C3, and the central unsaturated C_3 system features a typically allenoic distortion of its substituents from planarity. The structures of the strongly distorted cyclic allene derivatives are nonplanar and contain a chiral center (C1) and a chiral axis. It exists as a mixture of two diastereoisomers, with a *syn* or *anti* relationship of the bulky $B(C_6F_5)_2$ substituent at C1 with the substituent R at C2 (Scheme 5). This situation was found experimentally by dynamic NMR spectroscopy.

Additionally, the particular bonding characteristics of the chiral cycloallene were analyzed by DFT calculations. The calculated structure of the global minimum was in very good agreement with the X-ray crystal structure. The bond orders were calculated to be close to double bonds for C2–C3 (1.51) and C3–C4 (1.81). The low bond order of C1–C2 (1.12) supported the interpretation of the cycloallene character. For C3–C4, no triple bond was observed. *"The combination of experimental and computational work has shown an interesting electronic structure that can be regarded as a mixture of a distorted allene and a coordinated substituted butenyne."*



Scheme 5. Diastereomers of 1-hafnacyclopenta-2,3-dienes.

In the second paper,[7] the reaction of "Cp_2Zr" with a tetraaryl-substituted 1,2,3,4,5-hexapentaene to a 2,5-bis(alkylidene)-1-zirconacyclopent-3-yne was reported (Scheme 6). The isomeric 2-allenylidene-1-zirconacyclopent-3-yne was not formed, probably owing to the steric hindrance of the aryl groups in the α-position. This is probably the reason why analogous complexes of tetraarylsubstituted 1,2,3-butatrienes have not yet been obtained.[5d]

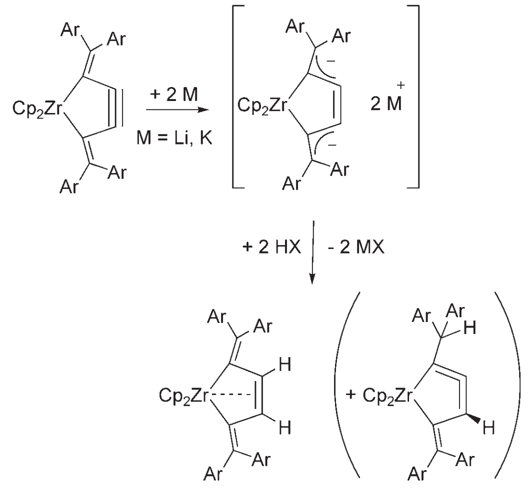


Scheme 6. Formation of 2,5-bis(alkylidene)-1-zirconacyclopent-3-yne.

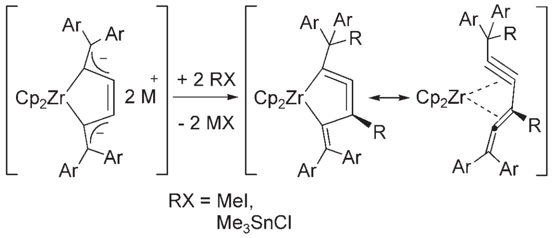
This complex reacted with lithium or potassium to give dianions, which were protonated to cyclopent-3-enes **3** as the major product (Scheme 7). This is the first example of formal hydrogenation of a cyclopent-3-yne **6** to give cyclopent-3-ene **3**. Additionally, the ^1H NMR spectra of the reaction mixture suggested the formation of cyclopenta-2,3-dienes **5** as a minor product.

Addition of iodomethane to the dianionic species afforded cyclopenta-2,3-dienes **5** selectively and in high yields by attack of one methyl group at the metallacycle and of a second at the benzylic position (Scheme 8). This reaction is a formal 1,4-addition to the starting pentatriene. The addition of α,α'-dibromo-*o*-xylene to the dianion yields the 1-zirconacyclopent-3-yne **6** (Scheme 9). Thus, formal transformation of cyclopent-3-ynes **6** to cyclopent-3-enes **3** and cyclopenta-2,3-dienes **5**, and of the latter back to cyclopent-3-ynes **6**, has been achieved.

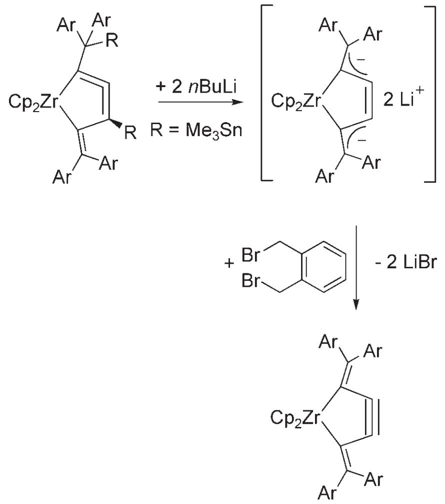
In the molecular structure, the plane of the cyclopenta-2,3-diene **5** is folded at the Zr–C2 bond (for the numbering, see Scheme 5). It can be described as a mixture of cyclopenta-2,3,4-triene **4** and cyclopent-3-ene **3**. The C3–C4 bond (1.286(4) Å) and the C2-C3-C4 angle (153.6(3)°) are in the same range as in cyclopenta-2,3,4-trienes **4**. The C2–C3



Scheme 7. Transformation of 2,5-bis(alkylidene)-1-zirconacyclopent-3-ynes via metallation to 2,5-bis(alkylidene)-1-zirconacyclopent-3-enes.

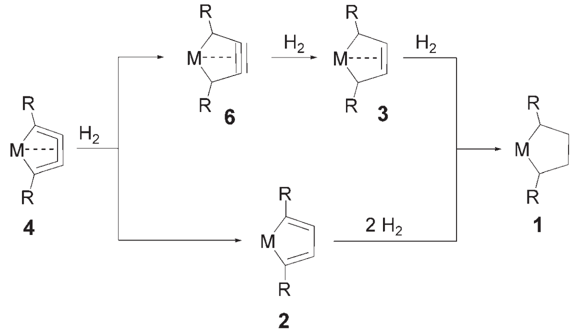


Scheme 8. Transformation of 2,5-bis(alkylidene)-1-zirconacyclopent-3-ynes to 1-zirconacyclopenta-2,3-dienes.



Scheme 9. Transformation of 1-zirconacyclopenta-2,3-dienes via metallation to 2,5-bis(alkylidene)-1-zirconacyclopent-3-ynes.

(1.372(4) Å) and C1−C2 (1.439(4) Å) bonds are close to those in cyclopent-3-ene **3**. From these results, the authors believe the C2−C3 bond to be a double bond, which is longer as a result of coordination to the metal.

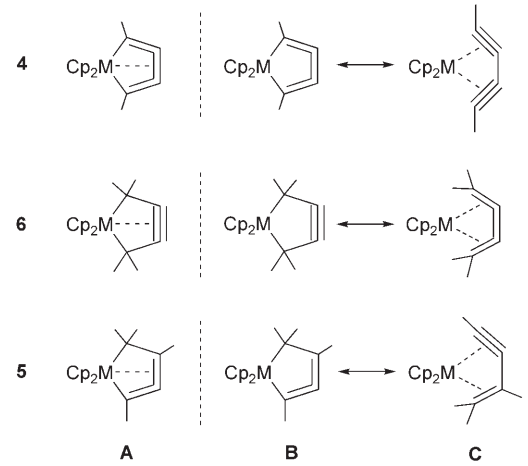


Scheme 10. Formation of 1-zirconacyclopentanes by stepwise hydrogenation of 1-metallacyclopenta-2,3,4-trienes.

The metallacycles **1**–**6** have different degrees of saturation, and their structural connection should allow the conversion from one into another (Scheme 10). For the hydrogenation starting from the metallacyclopent-3-yne **6**, an exothermic course of the hydrogenation reaction was calculated ($\mathbf{6}\rightarrow\mathbf{3}$: −24.7 kcal mol^{-1}, $\mathbf{3}\rightarrow\mathbf{1}$: −13.1 kcal mol^{-1}). Nevertheless, first experiments gave no evidence for this interconversion to occur.[3c,5d]

The most important result of these new investigations is the realization of predicted reactions and structures. Another feature is the chemical interconversion of different metallacycles. The general question then arises as to whether these related compounds should be regarded as η^4-π,π-1,3-diene, -diyne, or -enyne complexes, or unsaturated 1-metallacycles. However, it is not clear if and to what extent the unsaturated bonds interact with the metal.

From theoretical calculations on 1-metallacyclopenta-2,3,4-trienes **4** and 1-metallacyclopent-3-ynes **6**, Jemmis, Jiao and co-workers suggested donation from the double or triple bond to the metal (**A**, Scheme 11),[8] whereas Lin and Lam proposed the contribution of the η^4-π,π coordination mode (**C**).[9] Experimental studies by Suzuki et al. showed that structure **C** must contribute, although structure **B** is more important.[10] The same question is relevant to the related cyclopenta-2,3-dienes **5**. Suzuki suggested that this type of complex should be *"better described as η^4-1,3-enyne complexes rather than 1-zirconacyclopenta-2,3-dienes, although the latter might contribute to some extent."*



Scheme 11. Different descriptions of the bonding in the five-membered metallacycles presented herein.

Both papers, from Erker et al.[6] and from Suzuki et al.,[7] represent the enormous progress in the field of metallacycle chemistry as the basis for a theoretical understanding of selective stoichiometric and catalytic coupling reactions. For example, the dimerization of 1-alkynes[4c] and the polymerization of acetylene[11] could proceed via an oxidative addition to hydridoacetylides [$Cp_2M(H)(C{\equiv}CH)$], insertion of a further alkyne to yield [$Cp_2M(CH{=}CH_2)(C{\equiv}CH)$], coupling to but-1-en-3-ynes ($H_2C{=}CH{-}C{\equiv}CH$), and formation of cyclopenta-2,3-dienes **5**, which are capable of further insertions.

It is plausible to extend the results from unusual all-carbon 1-metallacyclopentynes to the analogous complexation of 1,3-heterobutatrienes, leading to 1-metalla-2,5-heterocyclopent-3-ynes.[3c] In such reactions, the formation of 1,3-heterocumulenes, such as $RN{=}C{=}C{=}NR$ or "$O{=}C{=}C{=}O$" could proceed by coupling of isonitriles or carbon monoxide and thus offer new perspectives for reaction pathways.

In summary, the possible isolation and often low reactivity of these strained compounds is surprising, which speaks for the structure **C** and interactions of the unsaturated bonds with the metal to delocalization.[8a] Purely carbon five-membered rings of this type have not been reported or were trapped only as short-lived species. In contrast, the metallacycles **1**–**6** are very stable at rom temperature under argon, and in some cases show unexpectedly poor reactivity.[3c]

Nevertheless, despite the progress, there is a strong need for further combination of experimental and computational work to understand the bonding of all of these unusual structures. In the two publications presented herein, the first important steps in this direction have been carried out.

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[1] R. D. Köhn, *Angew. Chem.* **2008**, *120*, 251–253; *Angew. Chem. Int. Ed.* **2008**, *47*, 245–247, and references therein.

[2] Valences are defined herein as the number of substituents that are in principle possible at the ring carbon atoms.

[3] For reviews, see: a) U. Rosenthal, *Angew. Chem.* **2004**, *116*, 3972–3977; *Angew. Chem. Int. Ed.* **2004**, *43*, 3882–3887; b) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, *Organometallics* **2005**, *24*, 456–471; c) U. Rosenthal, V. V. Burlakov, M. A. Bach, T. Beweries, *Chem. Soc. Rev.* **2007**, *36*, 719–728; d) N. Suzuki, *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 347–357, and references therein.

[4] a) G. Erker, G. Kehr, R. Fröhlich, *Adv. Organomet. Chem.* **2004**, *51*, 109–162; b) H. Yasuda, A. Nakamura, *Angew. Chem.* **1987**, *99*, 745–764; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 723–742; c) P. Štěpnička, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta, K. Mach, *Organometallics* **1999**, *18*, 4869–4880, and references therein.

[5] a) N. Suzuki, M. Nishiura, Y. Wakatsuki, *Science* **2002**, *295*, 660–663; b) N. Suzuki, N. Aihara, H. Takahara, T. Watanabe, M. Iwasaki, M. Saburi, D. Hashizume, T. Chihara, *J. Am. Chem. Soc.* **2004**, *126*, 60–61; c) N. Suzuki, T. Watanabe, T. Hirose, T. Chihara, *J. Organomet. Chem.* **2007**, *692*, 5317–5321; d) M. A. Bach, PhD thesis, University of Rostock, **2007**.

[6] J. Ugolotti, G. Dierker, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *Angew. Chem.* **2008**, *120*, 2662–2665; *Angew. Chem. Int. Ed.* **2008**, *47*, 2622–2625.

[7] N. Suzuki, D. Hashizume, H. Koshino, T. Chihara, *Angew. Chem.* **2008**, *120*, 5276–5280, *Angew. Chem. Int. Ed.* **2008**, *47*, 5198–5202.

[8] a) E. D. Jemmis, A. K. Phukan, H. Jiao, U. Rosenthal, *Organometallics* **2003**, *22*, 4958–4965; b) E. D. Jemmis, A. K. Phukan, K. T. Giju, *Organometallics* **2002**, *21*, 2254–2261.

[9] K. C. Lam, Z. Lin, *Organometallics* **2003**, *22*, 3466–3470.

[10] D. Hashizume, N. Suzuki, T. Chihara, *Chem. Commun.* **2006**, 1233–1235.

[11] U. Rosenthal, P. Arndt, W. Baumann, V. V. Burlakov, A. Spannenberg, *J. Organomet. Chem.* **2003**, *670*, 84–96.