

# Reviews

## Five-Membered Titana- and Zirconacyclocumulenes: Stable 1-Metallacyclopenta-2,3,4-trienes<sup>†</sup>

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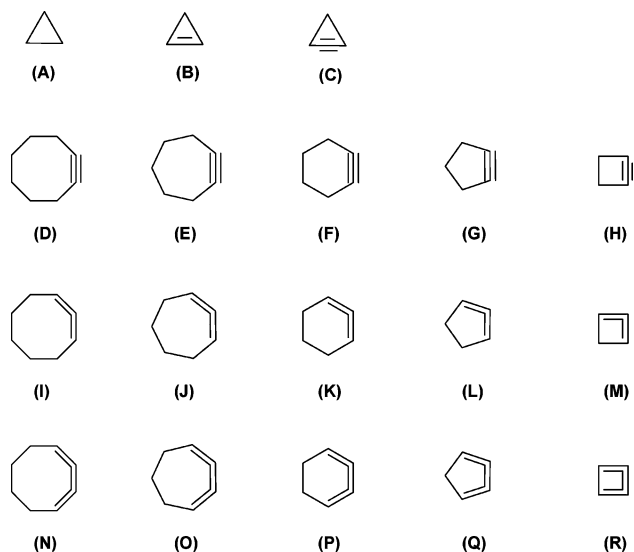
The rather exotic and uncommon five-membered metallacyclocumulenes (1-metallacyclopenta-2,3,4-trienes)  $\text{Cp}'_2\text{M}(\eta^4\text{-RC}_4\text{R})$  ( $\text{Cp}'$  = substituted  $\eta^5$ -cyclopentadienyl) are formed by “cis” complexation of titanocene or zirconocene fragments with 1,3-butadiynes or by coupling of two  $\sigma$ -acetylide groups in the coordination sphere of the metals. Examples of these complexes,  $\text{Cp}_2\text{M}(\eta^4\text{-RC}_4\text{R})$  ( $\text{M} = \text{Zr}$ ,  $\text{R} = t\text{-Bu}$ ;  $\text{M} = \text{Ti}$ ,  $\text{R} = t\text{-Bu}$ ,  $\text{R} = \text{Ph}$ ),  $\text{Cp}^*_2\text{M}(\eta^4\text{-RC}_4\text{R}')$  ( $\text{M} = \text{Zr}$ ,  $\text{R} = \text{R}' = \text{Me}_3\text{Si}$ ,  $\text{Me}$ ,  $\text{Ph}$ ,  $t\text{-BuMe}_2\text{Si}$ ;  $\text{R} = t\text{-Bu}$ ,  $\text{R}' = \text{C}\equiv\text{C}-t\text{-Bu}$ ),  $(\eta^6\text{-C}_5\text{H}_5\text{BX})_2\text{Zr}(\eta^4\text{-RC}_4\text{R})$  ( $\text{X} = i\text{-Pr}_2\text{N}$ ,  $\text{R} = \text{Ph}$ ;  $\text{X} = \text{Ph}$ ,  $\text{R} = \text{Ph}$ ,  $\text{Et}$ ),  $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}-t\text{-Bu})\text{Ti}(\eta^4\text{-RC}_4\text{R})$  ( $\text{R} = t\text{-Bu}$ ,  $\text{SiMe}_3$ ), and  $[\text{Cp}_2\text{Zr}]_3[1,3,5\text{-}(\eta^4\text{-}t\text{-BuC}_4)_3\text{C}_6\text{H}_3]$ , are discussed with regard to their genesis, synthesis, dynamics, structures, and bonding. These compounds are compared with the also uncommon and very similar five-membered metallacyclopentynes (1-metallacyclopent-3-yne)s  $\text{Cp}'_2\text{M}(\eta^4\text{-R}_2\text{C}_4\text{R}_2)$  ( $\text{M} = \text{Zr}$ :  $\text{Cp}' = \text{Cp}$ ,  $\text{R}_2 = t\text{-Bu/H}$ ,  $\text{Me}_3\text{Si/H}$ ,  $\text{H}_2$ ;  $\text{Cp}' = t\text{-BuC}_5\text{H}_4$ ,  $\text{R}_2 = \text{H}_2$ ;  $\text{M} = \text{Ti}$ :  $\text{Cp}' = \text{Cp}$ ,  $\text{R}_2 = \text{H}_2$ ) formed by analogous “cis” complexation of 1,2,3-butatrienes, in terms of their chemistry, structures, and bonding. Furthermore, reactions in which metallacyclocumulenes were assumed to be intermediates are described, together with the reactivity of metallacyclocumulenes toward different complexes and substrates: e.g. metal complexes, carbon dioxide, diisobutylaluminum hydride, and tris(pentafluorophenyl)borane. Upon complexation with a second transition-metal complex fragment either bridging formal  $\mu$ -“cis” or  $\mu$ -“trans” complexes of 1,3-butadiynes and 1,2,3-butatrienes were formed.

### Introduction

Structural limitations in cyclic hydrocarbons have been a longstanding challenge, leading to interesting molecules with sometimes abnormal geometric parameters and reactions.<sup>1</sup> Incorporation of cumulene double bonds or of triple bonds into small carbocyclic rings leads to an enormous ring strain, as a result of the large angle deformation of the normally linear  $\text{C}=\text{C}=\text{C}$  and  $\text{C}=\text{C}=\text{C}=\text{C}$  or  $\text{CC}\equiv\text{CC}$  arrangements in the open-chain compounds. This is the reason, why in contrast to stable cyclopropane (**A**) and cyclopropene (**B**) as isolable and very reactive compounds, cyclopropyne (**C**) does not exist (Chart 1).

In the series of *cycloalkynes*,<sup>1f</sup> cyclooctyne (**D**) is the smallest compound which is stable at room temper-

Chart 1



ature.<sup>2a</sup> Cycloheptyne (**E**) polymerizes at room temperature and is stable at lower temperature for only several hours. Cyclohexyne (**F**) and cyclopentyne (**G**) are highly reactive and have been detected only as intermediates or in inert matrices. Cyclopropyne and cyclobutyne (**H**) are unknown. For *cyclic allenes*<sup>1f</sup> the unsubstituted

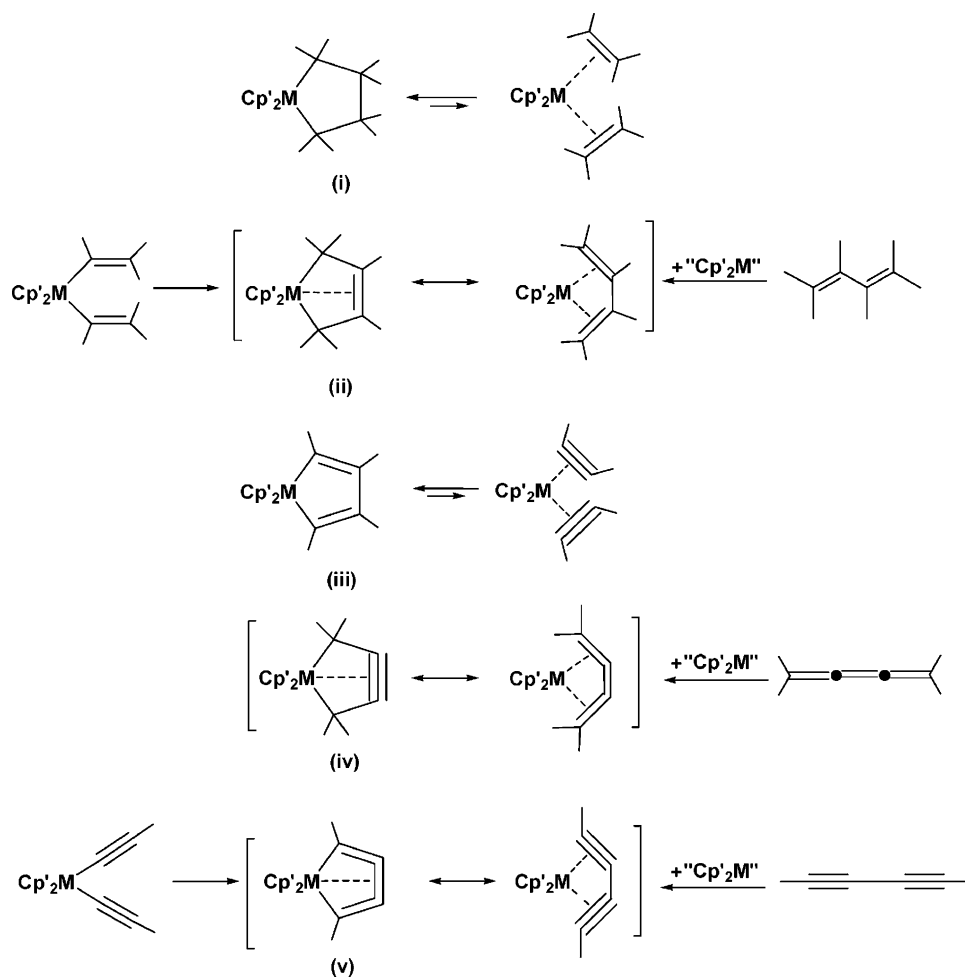
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<sup>†</sup> Dedicated to Prof. Dr. Günther Wilke on the occasion of his 80th birthday.

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(1) Selected reviews: (a) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189. (b) Gleiter, R.; Merger, R. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 1995; p 284. (c) Jones, W. M.; Klosin, J. *Adv. Organomet. Chem.* **1998**, *42*, 147. (d) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111. (e) Zahradnik, R.; Hobza, P.; Burcl, R.; Hess, B. A.; Radziszewski, J. G. *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 335. (f) Komarov, I. V. *Russ. Chem. Rev.* **2001**, *70*, 991 and references therein. (g) Low, P. J.; Bruce, M. I. *Adv. Organomet. Chem.* **2002**, *48*, 71. (h) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 159.

Scheme 1



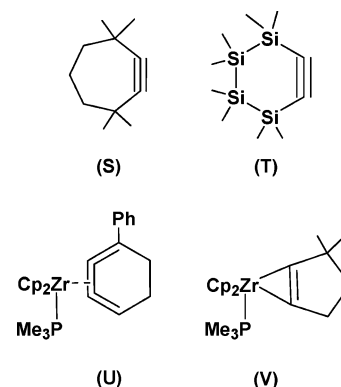
cycloocta-1,2-diene (**I**) has not yet been isolated in the pure state. Cyclohepta-1,2-diene (**J**) exists only when it is stabilized by complexation to metals, and cyclohexa-1,2-diene (**K**) was detected as a short-lived intermediate. Cyclopenta-1,2-diene (**L**) has been the subject of computations, and cyclobuta-1,2-diene (**M**) is unknown.

The smallest unsubstituted cyclic 1,2,3-triene (*cyclocumulene* with the buta-1,2,3-triene unit), stable at room temperature, to be experimentally described is cycloocta-1,2,3-triene (**N**), whereas cyclohepta-1,2,3-triene (**O**) and cyclohexa-1,2,3-triene (**P**) are highly reactive intermediates.<sup>2b</sup> The smaller cyclopenta-1,2,3-triene (**Q**) and cyclobuta-1,2,3-triene (**R**) have not been prepared.

There are many examples of the stabilization of such small-ring systems by substitution and/or complexation.<sup>3</sup> For example, the unstable cycloheptyne (**E**) ring became isolable when four methyl groups were introduced in the  $\alpha$ -positions to give 3,3,7,7-tetramethylcycloheptyne (**S**) (Chart 2).<sup>3a</sup>

In addition to this effect, the *substitution* of carbon atoms in the ring by heteroatoms can reduce the ring strain by the longer heteroatom-carbon bonds, as shown for the 1,2,3,4-tetrasilacyclohex-5-yne (**T**).<sup>3b</sup> Five-membered hetarynes and heterocyclocumulenes are not so unusual in organic chemistry.<sup>4</sup> They had been suggested

Chart 2



as reactive intermediates when Wittig in the early 1960s discussed such species.<sup>4a</sup> More recently 3,4-didehydrothiophenes<sup>4b</sup> and -pyrroles<sup>4c</sup> were investigated by Wong

(3) (a) Krebs, A.; Kimling, H. *Angew. Chem.* **1971**, *83*, 540; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509. (b) Ando, W.; Hojo, F.; Sekigawa, S.; Nakaayama, N.; Shimizu, T. *Organometallics* **1992**, *11*, 1009. (c) Yin, J.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 8859. (d) Buchwald, S. L.; Lum, R. T.; Fisher, R. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 9113. (e) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem.* **1989**, *101*, 1349; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

(4) (a) Wittig, G.; Wahl, V. *Angew. Chem.* **1961**, *73*, 492; *Angew. Chem., Int. Ed. Engl.* **1961**, *1*, 415. (b) Ye, X.-S.; Wong, H. N. C. *J. Org. Chem.* **1997**, *62*, 1940. (c) Liu, J.-H.; Chan, H.-W.; Xue, F.; Wang, Q.-G.; Mak, T. C.; Wong, H. N. C. *J. Org. Chem.* **1999**, *64*, 1630. (d) Cullen, W. R.; Rettig, S. J.; Zheng, T. *Organometallics* **1992**, *11*, 828 and references therein.

(2) (a) Blomquist, T.; Liu, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 2153. (b) Hernandez, S.; Kirchoff, M. M.; Swartz, S. G.; Johnson, R. P. *Tetrahedron Lett.* **1996**, *37*, 4907.

and co-workers, who were able to trap such five-membered heterocyclocumulenes containing sulfur and nitrogen by reactions with furan, acrylonitrile, and benzene.

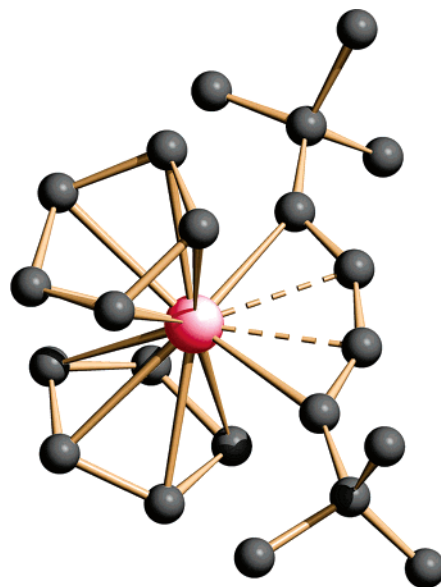
References to ferrocene,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_3)$ , containing a coordinated unsubstituted cyclopentadiene are limited to reports which suggest that this species might be involved as an intermediate in reactions.<sup>4d</sup> *External complexation* of the unsaturated  $\text{C}=\text{C}=\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$  bonds and the rehybridization effected thereby can effectively reduce the ring strain, as shown by the examples of a substituted cyclohexa-1,2,3-triene (**U**)<sup>3c</sup> and a substituted cyclopentadiene (**V**).<sup>3d,e</sup> *Internal complexation* of  $\text{C}=\text{C}=\text{C}=\text{C}$  by metals in the ring is the main stabilizing effect in the case of the titana- and zirconacyclocumulenes described in this review, according to experimental<sup>5,9</sup> and theoretical results.<sup>6</sup> This is what stabilizes the unusual small-ring systems. Internal complexation of the  $\text{C}\equiv\text{C}$  bond also stabilizes the similar metallacyclopentynes.<sup>7</sup> The existence and the formation of five-membered titana- and zirconacyclocumulenes (1-metallacyclopenta-2,3,4-trienes) should be discussed<sup>5h</sup> in the context of other *symmetrically substituted* five-membered titana- and zirconacycles,<sup>8</sup> all of which are relevant to stoichiometric and catalytic C–C coupling and cleavage reactions of unsaturated molecules (Scheme 1).

These complexes in Scheme 1 are *1-metallacyclopentanes* (**i**; obtained by oxidative coupling of two olefins),<sup>8a</sup> *1-metallacyclopent-3-enes* (**ii**; synthesized by complexation of 1,3-butadienes<sup>8b–d</sup> or by reductive elimination of two anionic vinyl groups),<sup>8e–g</sup> *1-metallacyclopent-2,4-dienes* (**iii**; prepared by oxidative coupling of two alkenes),<sup>8h,i</sup> *1-metallacyclopent-3-yne* (**iv**; formed by complexation of butatrienes),<sup>7</sup> and *1-metallacyclopent-2,3,4-trienes* (**v**, produced by complexation of 1,3-butadiynes or by reductive elimination of two anionic acetylide groups).<sup>5,10</sup>

(5) *Reviews and book contributions*: (a) Ohff, A.; Pulst, S.; Lefebvre, C.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (b) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (c) Rosenthal, U.; Burlakov, V. V. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; Chapter 10, p 355. (d) Rosenthal, U.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A. *Organometallics* **2003**, *22*, 884. (e) Rosenthal, U.; Arndt, P.; Baumann, W.; Burlakov, V. V.; Spannenberg, A. *J. Organomet. Chem.* **2003**, *670*, 84. (f) Rosenthal, U. *Angew. Chem.* **2003**, *115*, 1838; *Angew. Chem., Int. Ed.* **2003**, *42*, 1794. (g) Spannenberg, A.; Arndt, P.; Baumann, W.; Rosenthal, U. *J. Organomet. Chem.* **2003**, *683*, 261. (h) Rosenthal, U. *Angew. Chem.* **2004**, *116*, 3972; *Angew. Chem., Int. Ed.* **2004**, *43*, 3882. (i) Rosenthal, U. In *Modern Acetylene Chemistry II—Chemistry, Biology, and Material Science*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 4, p 139.

(6) *Calculations*: (a) Pavan Kumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125. (b) Jemmis, E. D.; Giju, K. T. *Angew. Chem.* **1997**, *109*, 633; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 606. (c) Jemmis, E. D.; Giju, K. T. *J. Am. Chem. Soc.* **1998**, *120*, 6952. (d) Jemmis, E. D.; Phukan, A. K.; Rosenthal, U. *J. Organomet. Chem.* **2001**, *635*, 204. (e) Jemmis, E. D.; Phukan, A. K.; Giju, K. T. *Organometallics* **2002**, *21*, 2254. (f) Lam, K. C.; Lin, Z. *Organometallics* **2003**, *22*, 3466. (g) Jemmis, E. D.; Phukan, A. K.; Jiao, H.; Rosenthal, U. *Organometallics* **2003**, *22*, 4958. (h) Bachrach, S. M.; Gilbert, J. C. *J. Org. Chem.* **2004**, *69*, 6357. (i) Angus, R. O.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880.

(7) *Metallacyclopentynes*: (a) Suzuki, N.; Nishiura, M.; Wakatsuki, Y. *Science* **2002**, *295*, 660. (b) Suzuki, N.; Ahihara, N.; Takahara, H.; Watanabe, T.; Iwasaki, M.; Saburi, M.; Hashizume, D.; Chihara, T. *J. Am. Chem. Soc.* **2004**, *126*, 60. (c) Maercker, A.; Groos, A. *Angew. Chem.* **1996**, *108*, 216; *Angew. Chem., Int. Ed.* **1996**, *35*, 210. (d) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Parameswaran, P.; Jemmis, E. D. *Chem. Commun.* **2004**, 2074. (e) Suzuki, N.; Watanabe, T.; Hirose, T.; Chihara, T. *Chem. Lett.* **2004**, *33*, 1488. (f) Suzuki, N.; Watanabe, T.; Iwasaki, M.; Chihara, T. Submitted for publication in *Organometallics*. (g) Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. 7th North-German Colloquy of PhD Students of Inorganic Institutes, Hamburg, Germany, Sept 29–30, 2004; lecture 1.1.

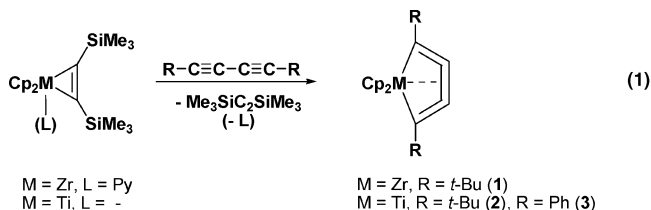


**Figure 1.** Molecular structure of the metallocene-cyclocumulene **1**.

### Stable Five-Membered Metallacyclocumulenes

**Preparation and Examples.** Ten years ago, in 1994, the first stable five-membered metallacyclocumulenes were reported.<sup>9a</sup> To date, 14 examples of these novel complexes are known, the compounds  $\text{Cp}_2\text{M}(\eta^4\text{-RC}_4\text{R})$  ( $\text{M} = \text{Zr}$ ,  $\text{R} = t\text{-Bu}$  (**1**);<sup>9a</sup>  $\text{M} = \text{Ti}$ ,  $\text{R} = t\text{-Bu}$  (**2**),<sup>9b</sup>  $\text{R} = \text{Ph}$  (**3**)<sup>9c,d</sup>),  $\text{Cp}^*\text{M}(\eta^4\text{-RC}_4\text{R}')$  ( $\text{M} = \text{Zr}$ ,  $\text{R} = \text{R}' = \text{Me}_3\text{Si}$  (**4**),<sup>9e</sup>  $\text{Me}$  (**5**),<sup>9f</sup>  $\text{Ph}$  (**6**),<sup>9e</sup>  $t\text{-BuMe}_2\text{Si}$  (**7**),<sup>9g</sup>  $\text{R} = t\text{-Bu}$ ,  $\text{R}' = \text{C}\equiv\text{C}-t\text{-Bu}$  (**8**)<sup>9h</sup>),  $(\eta^6\text{-C}_5\text{H}_5\text{BX})_2\text{Zr}(\eta^4\text{-RC}_4\text{R})$  ( $\text{X} = i\text{-Pr}_2\text{N}$ ,  $\text{R} = \text{Ph}$  (**9**),<sup>9i</sup>  $\text{X} = \text{Ph}$ ,  $\text{R} = \text{Ph}$  (**10**),<sup>9i</sup>  $\text{R} = \text{Et}$  (**11**)<sup>9i</sup>),  $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N}-t\text{-Bu})\text{Ti}(\eta^4\text{-RC}_4\text{R})$  ( $\text{R} = t\text{-Bu}$  (**12**),<sup>9j</sup>  $\text{SiMe}_3$  (**13**)<sup>9j</sup>), and  $[\text{Cp}_2\text{Zr}]_3[1,3,5\text{-}(\eta^4\text{-}t\text{-BuC}_4)_3\text{C}_6\text{H}_3]$  (**14**).<sup>9k</sup>

The five-membered zirconacyclocumulene  $\text{Cp}_2\text{Zr}(\eta^4\text{-}t\text{-BuC}_4\text{-}t\text{-Bu})$  (**1**) (1-zirconacyclopenta-2,3,4-triene,  $\eta^4$ -butadiyne complex) was produced in the reaction of  $\text{Cp}_2\text{Zr}(\text{pyridine})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  with the 1,3-butadiyne  $t\text{-BuC}\equiv\text{CC}\equiv\text{C}-t\text{-Bu}$  with elimination of pyridine and bis(trimethylsilyl)acetylene (eq 1).<sup>9a</sup> The molecular struc-

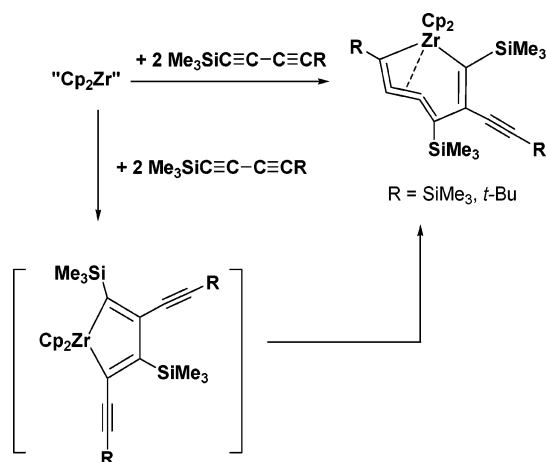


ture of complex **1** is shown in Figure 1.

Later the titanium analogues  $\text{Cp}_2\text{Ti}(\eta^4\text{-RC}_4\text{R})$  with  $\text{R} = t\text{-Bu}$ ,<sup>9b</sup>  $\text{Ph}$ <sup>9c,d</sup> also were obtained by the same procedure from  $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  and  $\text{RC}\equiv\text{CC}\equiv\text{CR}$  (eq 1). Among the other products of reactions of zirconocene with the  $\text{Me}_3\text{Si}$  substituted 1,3-butadiynes<sup>9a,l</sup>  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CR}$  ( $\text{R} = \text{Me}_3\text{Si}$ ,  $t\text{-Bu}$ ) were seven-membered cyclocumulenes (Scheme 2).<sup>9a,l,s</sup>

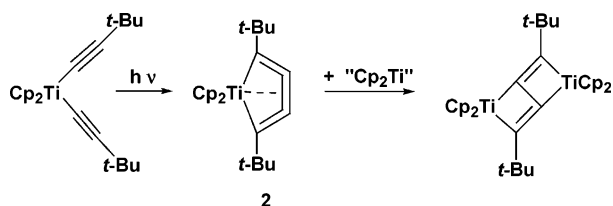
(8) *Examples*: (a) Takahashi, T.; Fischer, R.; Xi, Z.; Nakajima, K. *Chem. Lett.* **1996**, *241*, 357. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (c) Erker, G.; Kehr, G.; Fröhlich, R. *Adv. Organomet. Chem.* **2004**, *51*, 109. (d) Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (e) Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1984**, *268*, C7–C8. (f) Beckhaus, R.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1989**,

Scheme 2



Reactions of titanocene with  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  gave, depending on the stoichiometry used, only coupling or cleavage products, but no titanacyclocumulenes.<sup>9b</sup> Nevertheless, titanacyclocumulenes must be assumed to be intermediates in some of these reactions (see below).<sup>5</sup> It is of interest that irradiation of simple titanium bis(acetylides), such as  $\text{Cp}_2\text{Ti}(\sigma\text{-C}\equiv\text{C-}t\text{-Bu})_2$ , also can produce exotic five-membered titanacyclocumulenes,  $\text{Cp}_2\text{Ti}(\eta^4\text{-}t\text{-BuC}_4\text{-}t\text{-Bu})$  (**2**) in this case (Scheme 3), which was detected by NMR spectroscopy as an intermediate which rapidly reacted with additional titanocene "Cp<sub>2</sub>Ti" to give a complex with a bridging 1,3-butadiyne,  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2(1,3):\eta^2(2,4)\text{-}t\text{-Bu-C}_2\text{C}_2\text{-}t\text{-Bu}]$  (see below, Schemes 12 and 25).<sup>9m</sup> For this reason, this reaction cannot be used preparatively to synthesize titanacyclocumulenes. It remains unclear whether it proceeds via the complex  $[\text{Cp}_2\text{Ti}(\sigma\text{-C}\equiv\text{C-}t\text{-Bu})]$  or via the fragment "Cp<sub>2</sub>Ti" and the radical  $[\cdot\text{C}\equiv\text{C-}t\text{-Bu}]$ .

Scheme 3

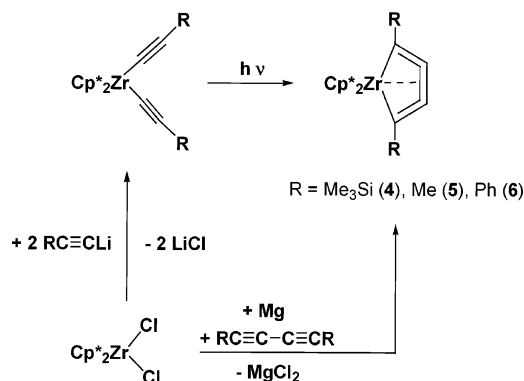


In principle, such a coupling of acetylides to 1,3-butadiynes is very common in organometallic chemistry. Typically, it is used in organic synthesis as the Glaser reaction.<sup>10a,b</sup> This type of reaction in which 1,3-butadiyne complexes are formed upon irradiation was first postulated by Frömberg<sup>10c</sup> in his Ph.D. dissertation in 1986 and was later found by Erker et al.<sup>10d-f</sup> to occur also under the catalytic influence of certain Lewis acids (see below).

Exposure of the decamethylzirconocene complexes  $\text{Cp}^*_2\text{Zr}(\sigma\text{-C}\equiv\text{CR})_2$  ( $\text{R} = \text{Ph}, \text{SiMe}_3, \text{Me}$ ) to sunlight resulted in C-C coupling of the alkynyl groups to give the zirconacyclocumulenes  $\text{Cp}^*_2\text{Zr}(\eta^4\text{-RC}_4\text{R})$  ( $\text{R} = \text{Ph}, \text{SiMe}_3, \text{Me}$ ) in high yields (perhaps via the formation and complexation of the 1,3-butadiynes) (Scheme 4).<sup>9e</sup> The deca-

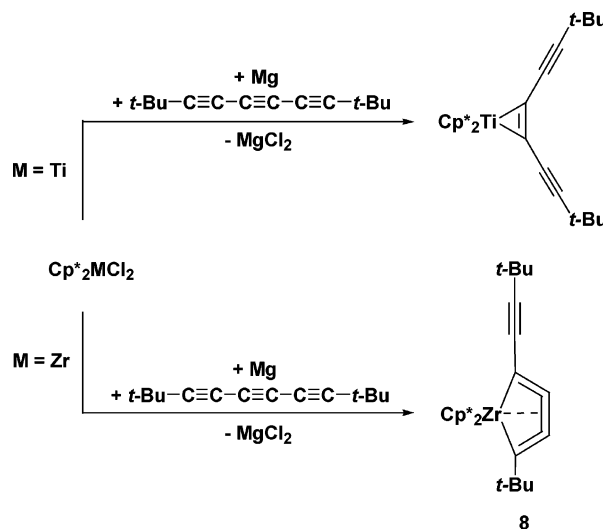
methylzirconocene complexes **4–6** also were prepared by the reduction of  $\text{Cp}^*_2\text{ZrCl}_2$  with magnesium in the presence of the corresponding diynes (Scheme 4).<sup>9e</sup>

Scheme 4



The formation of the 1,3-butadiyne complexes (**v**) by coupling of two geminal acetylides is similar to that of 1,3-butadiene complexes (**ii**) by the reductive elimination of two vinyl groups (Scheme 1).<sup>8e-g</sup> Formed by coupling of two anions, both of these metallacycles were calculated to be thermodynamically more stable in comparison to the corresponding starting materials  $[\text{Cp}_2\text{M}(\text{CH}=\text{CHR})_2]$ <sup>11</sup> and  $[\text{Cp}_2\text{M}(\text{C}\equiv\text{CR})_2]$ .<sup>6c</sup> With the hexatriyne  $t\text{-Bu-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{C-}t\text{-Bu}$  the unsymmetrically substituted zirconacyclocumulene  $\text{Cp}^*_2\text{Zr}(\eta^4\text{-}t\text{-BuC}_4\text{-C}\equiv\text{C-}t\text{-Bu})$  (**8**) was formed by the reduction of  $\text{Cp}^*_2\text{ZrCl}_2$  with magnesium in the presence of the diyne. In contrast, with  $\text{Cp}^*_2\text{TiCl}_2$  the titanacyclopentene  $\text{Cp}^*_2\text{Ti}(\eta^2\text{-}t\text{-BuC}\equiv\text{CC}_2\text{C}\equiv\text{C-}t\text{-Bu})$  was obtained (Scheme 5).<sup>9h</sup>

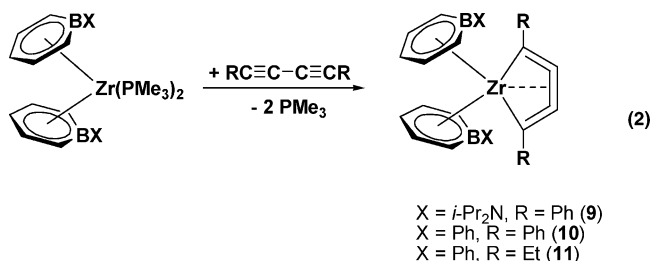
Scheme 5



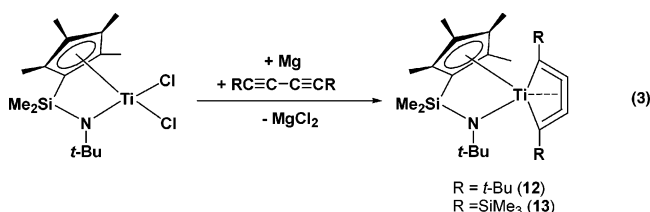
The first non-metallocene examples of such zirconacyclocumulenes,  $(\eta^6\text{-C}_5\text{H}_5\text{BX})_2\text{Zr}(\eta^4\text{-RC}_4\text{R})$  ( $\text{X} = i\text{-Pr}_2\text{N}, \text{R} = \text{Ph}$  (**9**),  $\text{X} = \text{Ph}, \text{R} = \text{Ph}$  (**10**),  $\text{R} = \text{Et}$  (**11**)), were reported by Ashe et al. as products of the reaction of bis(1-boratabenzene)bis(trimethylphosphine)zirconium(II) complexes with the 1,3-diynes  $\text{RC}\equiv\text{CC}\equiv\text{CR}$  (eq 2).<sup>9i</sup>

The first half-sandwich five-membered titanacyclocumulene complexes that contain linked amido-cyclopentadienyl ligands,  $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N-}t\text{-Bu})\text{Ti}(\eta^4\text{-RC}_4\text{R})$  with  $\text{R} = t\text{-Bu}$  (**12**),  $\text{Me}_3\text{Si}$  (**13**), were prepared by reaction of the dichloride  $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N-}t\text{-Bu})\text{TiCl}_2$

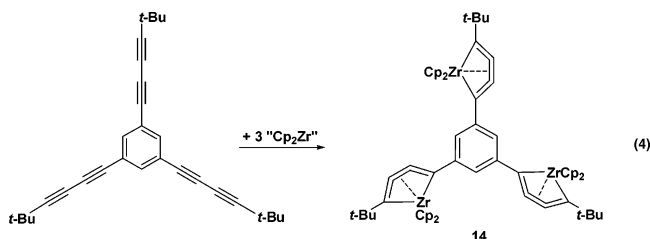
573, 195. (g) Böhme, U.; Thiele, K.-H.; Rufinska, A. *Z. Anorg. Allg. Chem.* **1994**, 620, 1455. (h) Sato, K.; Nishihara, Y.; Huo, S.; Xi, Z.; Takahashi, T. *J. Organomet. Chem.* **2001**, 633, 18. (i) Takahashi, T.; Ishikawa, M.; Huo, S. Q. *J. Am. Chem. Soc.* **2001**, 124, 388.



with magnesium in the presence of disubstituted 1,3-butadiynes (eq 3).<sup>9j</sup>

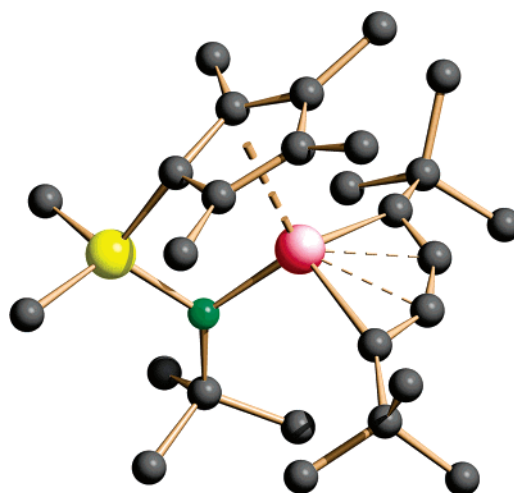


Three zirconacyclocumulene units in one molecule were realized in the complex [Cp<sub>2</sub>Zr]<sub>3</sub>[1,3,5-(*η*<sup>4</sup>-*t*-Bu-C<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>] (14), which was obtained in the reaction of 1,3,5-(*t*-BuC≡C≡C)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> with “Cp<sub>2</sub>Zr” generated from Cp<sub>2</sub>Zr(THF)(*η*<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) (eq 4).<sup>9k</sup>



**Structures.** Five-membered metallacyclocumulenes, the smallest isolated and structurally characterized cyclocumulenes, are very unusual. The molecular structure of complex 12 as a recent example is shown in

(9) *Cyclocumulenes*: (a) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem.* **1994**, *106*, 1678; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605. (b) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967. (c) Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *J. Organomet. Chem.* **1997**, *536*, 293. (d) Pellny, P.-M.; Burlakov, V. V.; Peulecke, N.; Baumann, W.; Spannenberg, A.; Kempe, R.; Francke, V.; Rosenthal, U. *J. Organomet. Chem.* **1999**, *578*, 125. (e) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 8313. (f) Kirchbauer, F. G.; Pellny, P.-M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 81. (g) Kirchbauer, F. G. Ph.D. Thesis, University of Rostock, 1999. (h) Pellny, P.-M.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2000**, *122*, 6317. (i) Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1999**, *18*, 4234. (j) Spannenberg, A.; Baumann, W.; Rosenthal, U. *Organometallics* **2002**, *21*, 1512. (k) Pellny, P.-M.; Burlakov, V. V.; Baumann, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1999**, *18*, 2906. (l) Hsu, D. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 10394. (m) Pulst, S.; Arndt, P.; Heller, B.; Baumann, W.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1996**, *108*, 1175; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1112. (n) Rosenthal, U.; Pulst, S.; Arndt, P.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *Organometallics* **1995**, *14*, 2961. (o) Hashmi, S.; Polborn, K.; Szeimies, G. *Chem. Ber.* **1989**, *122*, 2399. (p) Choukroun, R.; Zhao, J.; Lorber, C.; Cassoux, P.; Donnadiou, B. *Chem. Commun.* **2000**, 1511. (q) Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C 36. (r) Choukroun, R.; Donnadiou, B.; Lorber, C.; Pellny, P.-M.; Baumann, W.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 4505. (s) Kempe, R.; Ohff, A.; Rosenthal, U. *Z. Kristallogr.* **1995**, *210*, 707. (t) Rosenthal, U.; Ohff, A.; Tillack, A.; Baumann, W.; Görls, H. *J. Organomet. Chem.* **1994**, *468*, C4.



**Figure 2.** Molecular structure of the half-sandwich cyclocumulene 12.

Figure 2. Some selected structural data are listed in Table 1 together with the corresponding citations.

The structures of titana- and zirconacyclocumulenes show an almost planar arrangement of the metallacycle with three C–C double bonds, the central one of which is more elongated in comparison to the other two. This elongation is ascribed to the intramolecular interaction of the central C=C bond with the metal, which is close to that calculated for the cyclopenta-1,2,3-triene. In contrast, the corresponding angles in the complexes are different from those calculated for the all-carbon cycle (Table 2).<sup>1d</sup>

Theoretical calculations had shown that titana- and zirconacyclocumulenes are thermodynamically more stable than the isomeric bis(*σ*-acetylide) complexes.<sup>6c</sup> All four carbon atoms of the former diyne are viewed to have p orbitals occupied by one electron perpendicular to the plane of the cyclocumulene. The sp-hybridized internal C atoms possess additional p orbitals in that plane, which are used to establish donor bonding to the metal center. The calculated bond distances and angles are in good agreement with the experimental values.<sup>6c</sup> Additionally, Jemmis and co-workers used density functional theory (DFT) studies to understand the metallacyclocumulenes in light of the Dewar–Chatt–Duncanson model.<sup>6d,e</sup> For Ti and Zr the middle double bond is intact and there is no d→π\* back-bonding for the formal oxidation state +4, with a d<sup>0</sup> electron count. For a hypothetical “nickelacyclocumulene” the middle C–C bond is also longer than the other two C–C bonds, in this

(10) (a) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422. (b) Glaser, C. *Ann. Chem. Pharm.* **1870**, *154*, 136. (c) Frömberg, W. Ph.D. Thesis, University of Bochum, 1986. (d) Temme, B.; Erker, G.; Fröhlich, R.; Grell, M. *Angew. Chem.* **1994**, *106*, 1570; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480. (e) Ahlers, W.; Temme, B.; Erker, G.; Fröhlich, R.; Fox, T. *J. Organomet. Chem.* **1997**, *527*, 191. (f) Erker, G.; Venne-Dunker, S.; Kehr, G.; Kleigrew, N.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S. *Organometallics* **2004**, *23*, 4391.

(11) Beckhaus, R. *Angew. Chem.* **1997**, *109*, 694; *Angew. Chem., Int. Ed.* **1997**, *36*, 686.

(12) (a) Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3227. (b) Kirchbauer, F. G.; Pellny, P.-M.; Sun, H.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2001**, *20*, 5289. (c) Baumann, W.; Pellny, P.-M.; Rosenthal, U. *Magn. Reson. Chem.* **2000**, *38*, 515.


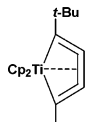

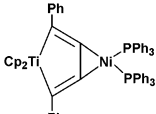
(13) Benn, H.; Wilke, G.; Henneberg, D. *Angew. Chem.* **1973**, *85*, 1052; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1001.

**Table 1.**  $^{13}\text{C}$  NMR and X-ray Data of Selected Metallacyclocumulenes  $\text{L}_2\text{M}(\eta^4\text{-RC}_4\text{R})$ 

	metallacyclocumulene <sup>a</sup> (ref)						
	1 (9a)	2 (9b)	4 (9e)	5 <sup>b</sup> (9f)	6 (9e)	11 <sup>c</sup> (9i)	12 (9j)
	$^{13}\text{C}$ NMR (ppm)						
C1	186.4	181.9	188.0	171.7	179.4	181.4	190.9
C2	105.5	94.7	144.5	111.5	118.4	108.3	142.6
	Bond Distances (Å)						
C1C2	1.28(1)	1.243(13)	1.291(6)	1.286(8)	1.296(4)	1.289(8)	1.279(8)
C3C4	1.29(1)	1.276(11)	1.293(6)	1.283(9)	1.305(5)	1.300(8)	1.270(8)
C2C3	1.31(1)	1.339(13)	1.337(6)	1.311(9)	1.327(4)	1.325(8)	1.358(8)
MC1	2.357(5)	2.298(10)	2.422(4)	2.325(5)	2.357(4)	2.308(6)	2.228(5)
MC4	2.307(5)	2.252(9)	2.426(5)	2.334(5)	2.345(4)	2.313(6)	2.209(6)
MC2	2.303(5)	2.213(9)	2.305(4)	2.307(5)	2.330(4)	2.304(7)	2.159(5)
MC3	2.306(5)	2.209(9)	2.307(4)	2.308(5)	2.328(4)	2.273(7)	2.169(5)
	Bond Angles (deg)						
MC1C2	71.7(3)	70.3(6)	69.2(3)	73.1(3)	72.8(2)	73.6	70.1(3)
MC4C3	73.7(3)	71.6(6)	69.2(3)	72.8(3)	73.1(2)	71.9	71.4(3)
C1C2C3	150.0(5)	150.0(10)	152.5(4)	148.2(5)	148.5(4)	145.8(7)	147.7(5)
C4C3C2	147.2(5)	147.8(10)	152.3(4)	148.6(5)	148.0(4)	149.7(8)	145.8(5)

<sup>a</sup> Numbering of the C atoms: C1 = C<sub>α</sub>, C2 = C<sub>β</sub>, C4 = C<sub>α'</sub>, C3 = C<sub>β'</sub>. <sup>b</sup> Bond lengths and angles for only one of the two molecules of the asymmetric unit. <sup>c</sup> Signal assignment uncertain in the NMR.

**Table 2.** Comparison of Structural Data of Five-Membered Titanacycles<sup>a</sup>

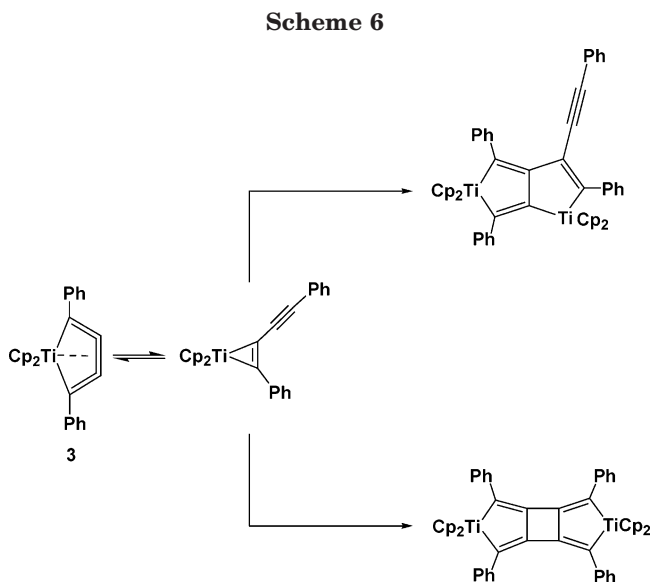
Compounds				
References	Calculated [6i]	2 [9b]	[7c]	[9m]
Bond distances [Å]				
C1C2	CH=C 1.335	1.243(13)	1.393(3)	1.316(7)
C3C4		1.276(11)		1.334(6)
C2C3	C=C 1.312	1.339(13)	1.248(4)	1.419(6)
TiC1	CH <sub>2</sub> -CH 1.576	2.298(10)	2.353(2)	2.124(4)
TiC4	No	2.252(9)		2.118(5)
TiC2	No	2.213(9)	2.202(2)	2.325(4)
TiC3	No	2.209(9)		2.340(5)
Angles [°]				
TiC1C2	CH <sub>2</sub> -CH=C 101.20	70.3(6)	66.4(1)	81.4(3)
TiC4C3		71.6(6)		82.0(3)
C1C2C3	CH=C=C 116.37	150.0(10)	151.7(1)	137.2(4)
C2C3C4		147.8(10)		135.4(4)

<sup>a</sup> Numbering of the C atoms refers to the four central C atoms of the butadiyne: C1 = C<sub>α</sub>, C2 = C<sub>β</sub>, C4 = C<sub>α'</sub>, C3 = C<sub>β'</sub>.

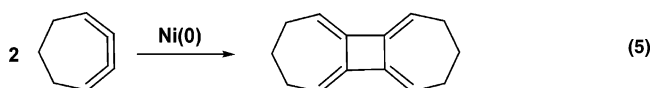
case showing a back-bonding interaction between the filled metal d orbitals and the in-plane empty  $\pi^*$  orbital of the middle C–C bond. By this calculation it is explained why the titanacyclocumulene dimerizes to a titanium-substituted radialene (Scheme 6), whereas for the “nickelacyclocumulene” a bis( $\mu$ -butadiyne) complex was obtained.<sup>6d</sup> Density functional theory studies of the energetics of the metal-free C<sub>5</sub>H<sub>4</sub> cyclocumulene, the alkynylcyclopropene, the dialkynylmethane, and their organometallic analogues obtained by replacing the CH<sub>2</sub> groups by the metallocenes Cp<sub>2</sub>Ti and Cp<sub>2</sub>Zr showed that the relative energies of the compounds are dra-

matically altered in the transition-metal analogues.<sup>6e</sup> The metallacyclocumulenes as  $\eta^4$  complexes are comparable in energy to the alkynyl-substituted metallacyclopropenes as  $\eta^2$  complexes and the bis(alkynyl) complexes. The different metals in and substituents on the carbon skeleton help to fine tune the energetics. The described relative energies also explained the experimental observation that the titanacyclopropene structure is more favorable compared to the zirconacyclopropene. The bonding situations in the metallacyclocumulenes and the zirconacyclopentynes are very similar (see below).<sup>6e-g</sup>

**General Reaction Behavior.** In some reactions of the metallacyclocumulenes an equilibrium between an  $\eta^4$  complex (metallacyclocumulene) and an  $\eta^2$  complex (metallacyclopropene) is evident.<sup>5,9c-f,h</sup> The two components of the equilibrium mixture can react with each other to afford an unsymmetric complex in which a titanacyclopentadiene is anellated to a titanacyclopentene (Scheme 6).<sup>9c,d,f</sup>



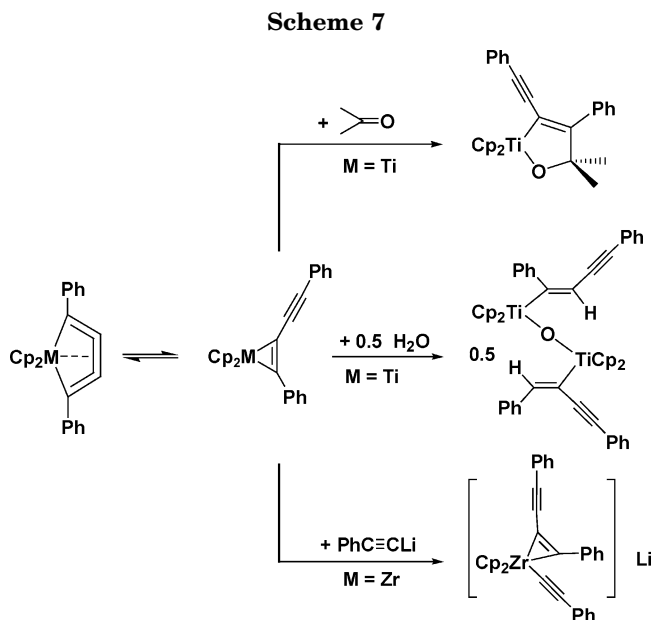
Formation of the latter can be rationalized in terms of an insertion of the internal double bond of the titanacyclocumulene into a Ti–C bond of the titanacyclopropene. The symmetrically substituted titanium radicalene is generated by formal dimerization of two titanacyclocumulene molecules. Similar complexes were also prepared with monomethylcyclopentadienyl ligands and Ph substituents<sup>9d</sup> as well as with Cp and Me as substituents.<sup>9f</sup> The analogous formation of an organic [4]radialene by catalytic dimerization of 1,2,3-cycloheptatriene induced by nickel(0) catalysts has been reported (eq 5).<sup>9o</sup>



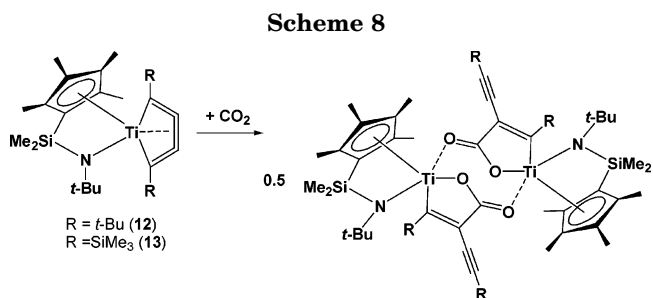
Whereas both members of the equilibrium react in the intermolecular coupling reaction of titanacyclocumulenes (Scheme 6), the products formed in the reaction of the titanacyclocumulene **3** with acetone and water

(14) Choukroun, R.; Donnadiou, B.; Zhao, J.; Cassoux, P.; Lepetit, C.; Silvi, B. *Organometallics* **2000**, *19*, 1901. (b) Danjoy, C.; Zhao, J.; Donnadiou, B.; Legros, J.-P.; Valade, L.; Choukroun, R.; Zwick, A.; Cassoux, P. *Chem. Eur. J.* **1998**, *4*, 1100. (c) Choukroun, R.; Cassoux, P. *Acc. Chem. Res.* **1999**, *32*, 494. (d) Mahiheu, A.; Miquel, Y.; Igau, A.; Majoral, J.-P. *Organometallics* **1997**, *16*, 3086. (e) Bredeau, S.; Delmas, G.; Pirio, N.; Richard, P.; Donnadiou, B.; Meunier, Ph. *Organometallics* **2000**, *19*, 4463. (f) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665. (g) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.-H.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842. (h) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2000**, *19*, 1198. (i) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Tillack, A.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1997**, *109*, 2728; *Angew. Chem., Int. Ed.* **1997**, *36*, 2615. (j) Bruce, M. L.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1997**, *536–537*, 93. (k) Yamazaki, S.; Taira, Z.; Yonemura, T.; Deeming, A. J.; Nakao, A. *Chem. Lett.* **2002**, 1174. (l) Yamazaki, S.; Taira, Z.; Yonemura, T.; Deeming, A. J. *Organometallics* **2005**, *24*, 20.

result only from the  $\eta^2$  complex (metallacyclopropene) (Scheme 7).<sup>9c</sup> The zirconacyclocumulene  $\text{Cp}_2\text{Zr}(\eta^4\text{-PhC}_4\text{-Ph})$  was assumed to be the intermediate in the reaction of  $\text{Cp}_2\text{ZrCl}_2$  with  $\text{PhC}\equiv\text{CLi}$ , which yielded the complex  $[\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2\text{-1:2-PhC}_2\text{-C}\equiv\text{CPh})\text{Li}]$  (Scheme 7). This was regarded as being indicative of an equilibrium between an  $\eta^2$  and an  $\eta^4$  complex.<sup>9p</sup>



The titanacyclocumulenes **12** and **13** reacted with carbon dioxide to give binuclear titanafuranones, products which were formed via the  $\eta^2$  complex (Scheme 8).<sup>9j</sup>

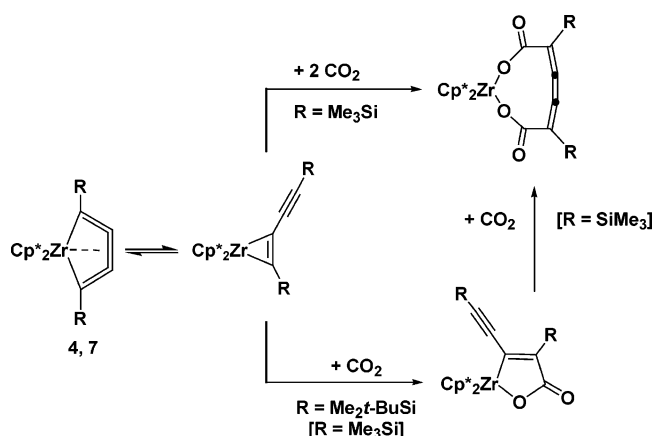


The zirconacyclocumulene with  $\text{Me}_3\text{Si}$  substituents **4** reacted with 2 equiv of carbon dioxide to form a cumulenic dicarboxylate by a formal 2-fold insertion into the  $\eta^4$  complex (Scheme 9, top), whereas only 1 equiv of carbon dioxide inserted into the corresponding zirconacyclocumulene containing  $\text{Me}_2\text{-}t\text{-BuSi}$  substituents **7** (Scheme 9, bottom).<sup>9e,g</sup> Nevertheless, it remains unclear whether **4** reacts as an  $\eta^4$  or an  $\eta^2$  complex. It seems possible that the  $\eta^2$  complex reacts first and that a further reaction of the alkynyl group in the position  $\alpha$  to the zirconium occurs (Scheme 9, right).<sup>5b,9e</sup>

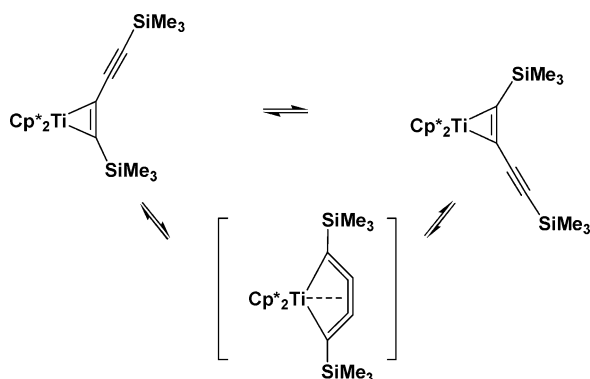
The interaction of a free triple bond with the larger metal center may lead with Zr (different from Ti) to the observed larger metallacycles (Scheme 2 and Scheme 9, right) or, alternatively, to an equilibrium between  $\eta^2$  and  $\eta^4$  coordination, as was shown for Ti in the case of the diyne complex  $\text{Cp}^*_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$  (Scheme 10).<sup>9e</sup>

For the triyne complex of Zr **8** this process can lead to a “sliding” of the “ $\text{Cp}^*_2\text{Zr}$ ” along the polyene chain

Scheme 9

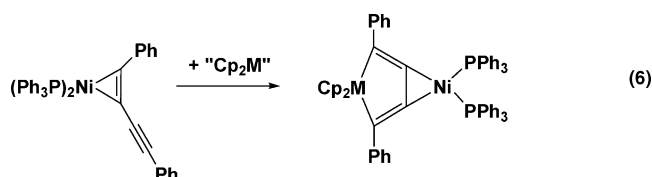


Scheme 10



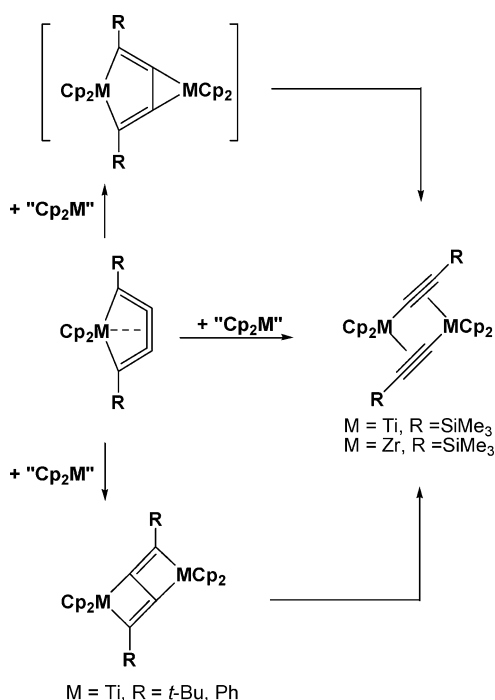
(Scheme 11).<sup>9h</sup> Also, the migration of the vanadocene “ $\text{Cp}_2\text{V}$ ” along the backbone of an octatetrayne was described.<sup>9r</sup> In all these cases more or less stable five-membered cyclocumulenes were assumed to participate as intermediates during these “sliding” processes.

**Complexation.** Depending on the nature of the metals and the substituents, some metallacyclocumulenes form stable complexes: e.g., with  $\text{Ni}(0)$ . For example,  $\pi$  complexes of the corresponding metallacyclocumulenes were isolated for  $\text{M} = \text{Ti}$  and  $\text{Zr}$  only with two phenyl substituents, which can be regarded as  $\text{Ni}(0)$ -cycloolefin complexes with two  $\text{Ph}_3\text{P}$  ligands of the type  $(\text{Ph}_3\text{P})_2\text{Ni}(\text{cycloolefin})$  (eq 6).<sup>9m</sup> Interestingly,



these compounds represent stable complexes of  $\eta^2$ -metallacyclopentatrienes. Such complexes are not stable

Scheme 12

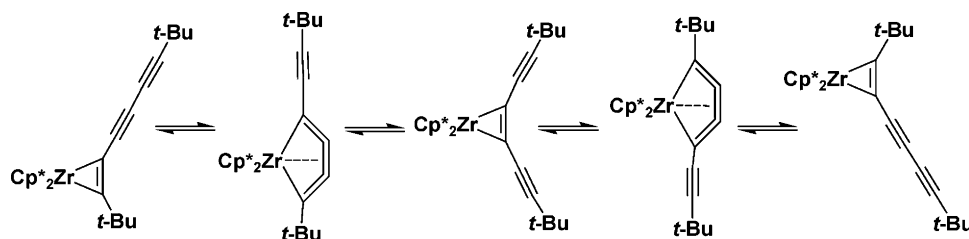


with two  $\text{Me}_3\text{Si}$  substituents or one  $\text{Ph}$  and one  $\text{Me}_3\text{Si}$  substituent.<sup>9n</sup>

Titanacyclocumulenes  $\text{Cp}_2\text{Ti}(\eta^4\text{-RC}_4\text{R})$  react with an additional titanocene, “ $\text{Cp}_2\text{Ti}$ ”, to give binuclear complexes with a bridging 1,3-butadiyne,  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2(1,3):\eta^2(2,4)\text{-}t\text{-Bu-C}_2\text{C}_2\text{-}t\text{-Bu}]$  (Scheme 12).<sup>5</sup> These complexes are important for two reasons. On one hand, the complex shown in eq 6 is a real proof for the metallacyclocumulene structure of the  $\eta^4$  complex. On the other hand, these compounds can be viewed as intermediates for further complexation and cleavage reactions to doubly  $\sigma,\pi$ -alkynyl-bridged homo- and heterobinuclear metal complexes (Scheme 12).<sup>9m,n,q</sup> It was shown by NMR and mass spectroscopy that the binuclear complexes  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2(1,3):\eta^2(2,4)\text{-RC}_2\text{C}_2\text{R}]$  can form unstable monomeric  $\text{Ti}(\text{III})$  monoacetylides  $[\text{Cp}_2\text{Ti}(\sigma\text{-C}\equiv\text{CR})]$ . Such  $\text{Ti}(\text{III})$  complexes are stable and isolable in the case of decamethyltitanocene and  $\text{Cp}^*_2\text{Ti}(\sigma\text{-C}\equiv\text{CR})$  ( $\text{R} = \text{Me}$ ,  $t\text{-Bu}$ ).<sup>12</sup> Nevertheless, it remains unclear whether the doubly  $\sigma,\pi$ -alkynyl bridged complexes are formed via the  $\eta^2$ -metallacyclopentatriene (“*cis*-butadiyne”) complexes (top) or the “*trans*-butadiyne” complexes (bottom) in the two options shown in Scheme 12.

The process of such a cleavage reaction of 1,3-butadiynes can be called also a *dichotomy*. To the best of our knowledge, in biology and astronomy the often-used term “dichotomy” (dichotomia,  $\delta\iota\chi\omicron\tau\omicron\mu\iota\alpha$  = cut in half), was first introduced in chemistry by Wilke and co-workers for the cleavage of 2-butyne in the formation

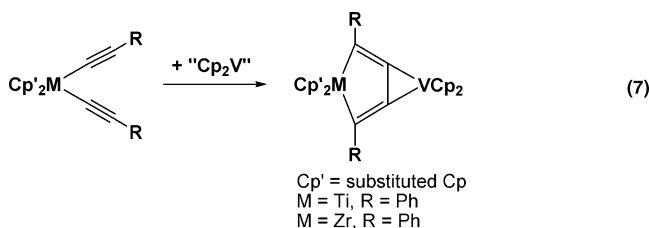
Scheme 11



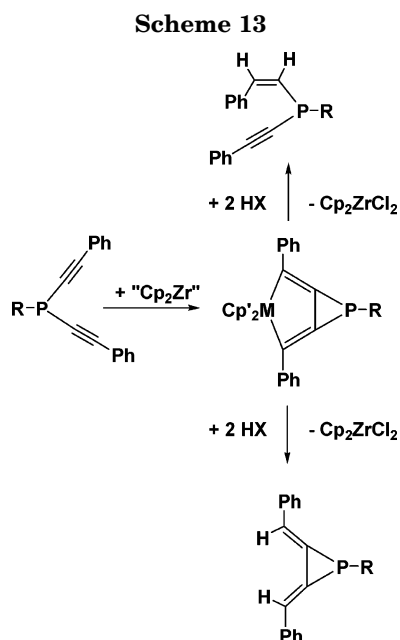


of pentamethylcyclopentadienyl ligands by  $\text{CrCl}_3/\text{Et}_3\text{-Al}$  mixtures.<sup>13</sup>

Meanwhile,  $\pi$  complexes of cyclocumulenes were reported also for other metals.<sup>14</sup> These complexes also were assumed to be intermediates in the C–C single bond cleavage reaction of butadiynes. Complexes of metallacyclocumulenes with “[ $\text{Cp}_2\text{V}$ ]”, “[ $\text{R}-\text{P}$ ]” and “[ $\text{R}_2\text{-Si}$ ]” are examples of this. According to Choukroun et al. the reaction of the bis(acetylide)  $\text{Cp}'_2\text{M}(\sigma\text{-C}\equiv\text{CR})_2$  ( $\text{Cp}'$  = differently monosubstituted Cp ligands,  $\text{M} = \text{Ti}$ ,  $\text{Zr}$ ) with vanadocene gives  $\text{Cp}_2\text{V}(\mu\text{-}\eta^2, \eta^4\text{-}(\text{RC}_4\text{R})\text{MCp}'_2)$  complexes (eq 7).<sup>14a-c</sup>



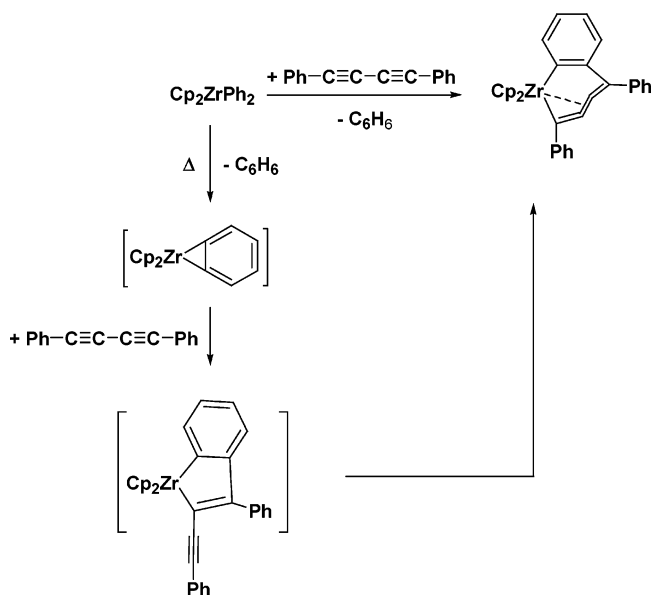
Majoral and co-workers found the reaction of bis(alkynyl)phosphines with zirconocene to yield the zirconacyclopentadiene phosphirane (Scheme 13).<sup>14d</sup> These cyclic systems in subsequent reactions with HCl gave, among other products, an alkenyl(alkynyl)phosphine and a phospharadialene.



Meunier et al. described the formation of a seven-membered zirconacyclocumulene in the reaction of the in situ formed zirconocene benzyne complex with 1,4-diphenyl-1,3-butadiyne (Scheme 14).<sup>14e</sup> The assumed intermediate with an alkynyl group as a substituent in the position  $\alpha$  to the zirconium should lead to ring enlargement of the metallacycle, similar to that shown in Schemes 2 and 9.

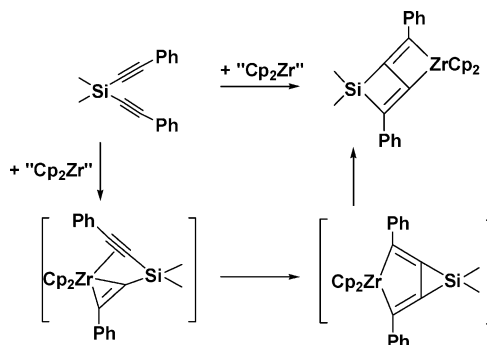
The intramolecular coupling of the alkynyl groups of bis(alkynyl)silanes mediated by zirconocene (Scheme 15) was reported by Takahashi and co-workers.<sup>14f,g</sup> Interestingly, the products formed in this reaction (Scheme 15, top right) are very similar to those which were obtained in the reactions of tetrakis(alkynyl)silanes<sup>14h</sup> and of

Scheme 14



tetraynes<sup>14i</sup> with titanocene and zirconocene, having all the structural elements of the binuclear titanocene complexes  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2(1,3):\eta^2(2,4)\text{-RC}_2\text{C}_2\text{R}]$  (Scheme 12), but with the combinations Zr/Si and Ti/Si instead of Ti/Ti.<sup>14h</sup> It was mentioned that silylenes form similar products with 1,3-diyne with Si/Si combinations.<sup>5d,14h</sup>

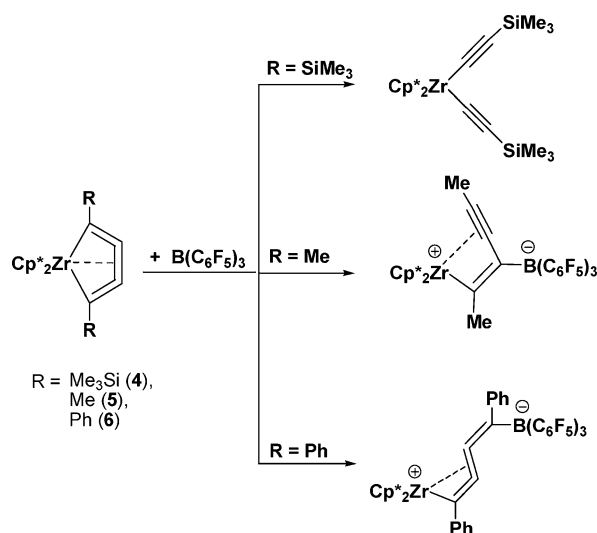
Scheme 15



**Reactions with Lewis Acids.** The five-membered zirconacyclocumulenes **4–6** each react in a different manner with  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 16).<sup>15a</sup> With **4** ( $\text{R} = \text{Me}_3\text{-Si}$ ) bond cleavage of the central carbon–carbon double bond of the cyclocumulene was found and the bis( $\sigma$ -alkynyl) complex  $\text{Cp}^*_2\text{Zr}(\sigma\text{-C}\equiv\text{CSiMe}_3)_2$  was formed. This reaction occurred catalytically with 10% of  $\text{B}(\text{C}_6\text{F}_5)_3$ , giving after 6 days a quantitative yield of the decamethylzirconocene diacetylide. In contrast to this reaction, in the case of **5** ( $\text{R} = \text{Me}$ ) the  $\text{B}(\text{C}_6\text{F}_5)_3$  attacked the  $\beta$ -C atom of the starting cumulene and the  $\text{C}_4$  chain remained intact, forming the complex  $\text{Cp}^*_2\text{Zr}\{\eta^3\text{-}1,3,4\text{-C}(\text{Me})\text{C}[\text{B}(\text{C}_6\text{F}_5)_3]\text{C}\equiv\text{CMe}\}$  with a hex-2-ene-4-yne-2-yl-3-[tris(pentafluorophenyl)borate] ligand. This reaction course was described in detail by Erker and his group<sup>10d-f</sup> also for the corresponding cyclocumulene that contained unsubstituted Cp ligands on Zr,  $\text{Cp}_2\text{Zr}(\eta^4\text{-MeC}_4\text{Me})$ . Very recently, the structure of  $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}\{\eta^3\text{-}1,3,4\text{-C}(\text{Me})\text{C}[\text{B}(\text{C}_6\text{F}_5)_3]\text{C}\equiv\text{CMe}\}$  was published as the first example of complexes of this type.<sup>10f</sup> The  $\text{C}_4$  chain also was not cleaved in complex **6** ( $\text{R} = \text{Ph}$ ), but  $\text{B}(\text{C}_6\text{F}_5)_3$  attacked the  $\alpha$ -C atom of the starting cumulene to yield

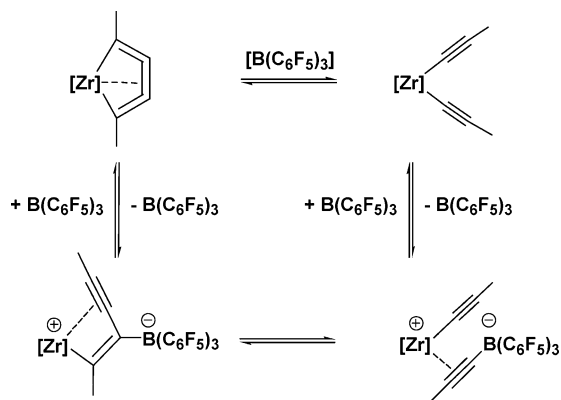
$\text{Cp}^*_2\text{Zr}\{\eta^3\text{-}1,2,3\text{-C(Ph)=C=C(Ph)[B(C}_6\text{F}_5)_3]\}$  with a 1,4-diphenylbuta-1,2,3-triene-1-yl-4-[tris(pentafluorophenyl)borate] ligand. This was the first example for an attack of such an electrophile at the  $\alpha$ -C atom of a cyclocumulene.

Scheme 16



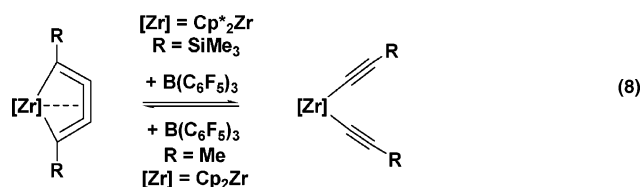
On the basis of these findings, the catalytic influence of  $\text{B(C}_6\text{F}_5)_3$  on C–C cleavage and coupling reactions could be described in terms of an equilibrium (Scheme 17) in which the reactions of five-membered zirconacyclocumulenes  $\text{Cp}'_2\text{Zr}(\eta^4\text{-}1,2,3,4\text{-RC}_4\text{R})$  ( $\text{Cp}' = \text{Cp}, \text{Cp}^*$ ) with  $\text{B(C}_6\text{F}_5)_3$  are strongly influenced by the  $\text{Cp}'$  ligands and the substituents R. Depending on the nature of R, for  $\text{Cp}^*$  either C–C bond cleavage to give a bis(alkynyl) complex ( $\text{R} = \text{Me}_3\text{Si}$ ) or reactions of the borane at the  $\beta$ -C ( $\text{R} = \text{Me}$ ) and  $\alpha$ -C atoms ( $\text{R} = \text{Ph}$ ) with formation of the zwitterionic complexes can occur.

Scheme 17



These products represent different steps of the C–C cleavage and the C–C coupling reactions. Whether in these systems zirconacyclocumulenes (by coupling) or bis(alkynyl) compounds (by cleavage) are obtained is determined by the choice of the  $\text{Cp}'$  ligand system and the substituent R: e.g., for  $\text{Cp}/\text{Me}$  the cycle<sup>10d</sup> and for  $\text{Cp}^*/\text{Me}_3\text{Si}$  the bis(alkynyl) complex is formed (eq 8).<sup>15a</sup>

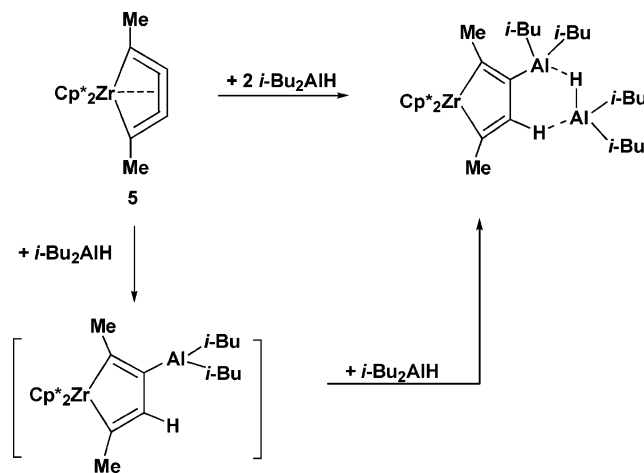
In summary, it should be pointed out that  $\text{B(C}_6\text{F}_5)_3$  can catalyze either C–C coupling or cleavage in such systems, but metallacyclocumulenes always are involved. Regarding the experimental results mentioned



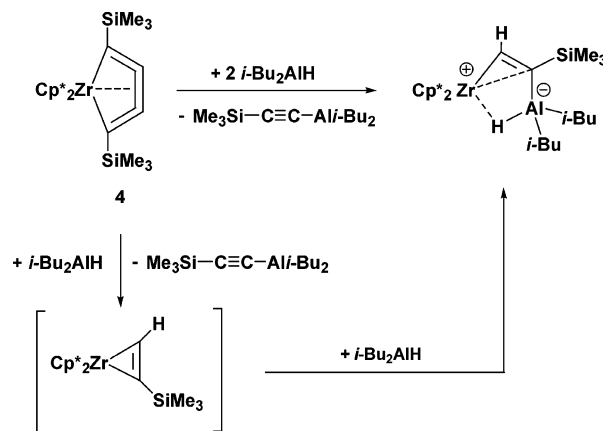
above and shown in Scheme 4<sup>9e</sup> and calculations<sup>6c</sup> of the coupling of acetylides to the thermodynamically more stable cyclocumulenes,<sup>6c</sup> these experiments show that for the  $\text{Me}_3\text{Si}$  substituent cleavage is the case.

The products of the reactions of the five-membered zirconacyclocumulenes 4–6 with  $i\text{-Bu}_2\text{AlH}$ <sup>15b</sup> can serve as models for the elementary reaction steps of the zirconocene-catalyzed hydroalumination of disubstituted buta-1,3-diyne  $\text{RC}\equiv\text{CC}\equiv\text{CR}$  and for the activation of zirconocene complexes in the catalytic polymerization of ethylene. The reactions of the zirconacyclocumulenes with  $i\text{-Bu}_2\text{AlH}$  start with a cis hydroalumination of the central double bond in which the intermediate formation of zirconacyclopentadienes with  $i\text{-Bu}_2\text{Al}$  substituents in the 3-position was assumed. These complexes were not isolated but subsequently stabilized in a different manner, depending on the substituents R used. For 5 ( $\text{R} = \text{Me}$ ), the intermediate reacts with a second molecule of  $i\text{-Bu}_2\text{AlH}$  to give a complex of the substituted zirconacyclopentadiene with  $i\text{-Bu}_2\text{AlH}$  (Scheme 18). The central C–C bond was cleaved in complex 4 ( $\text{R} = \text{Me}_3\text{Si}$ ) (“hydroaluminolysis”) with formation of the alkyne  $i\text{-Bu}_2\text{AlC}\equiv\text{CSiMe}_3$  and the alkyne complex  $[\text{Cp}^*_2\text{Zr}(\eta^2\text{-Me}_3\text{SiCCH})]$  (Scheme 19).

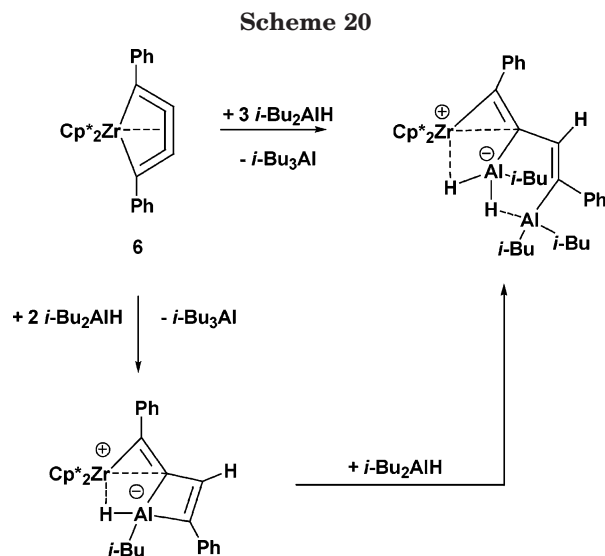
Scheme 18



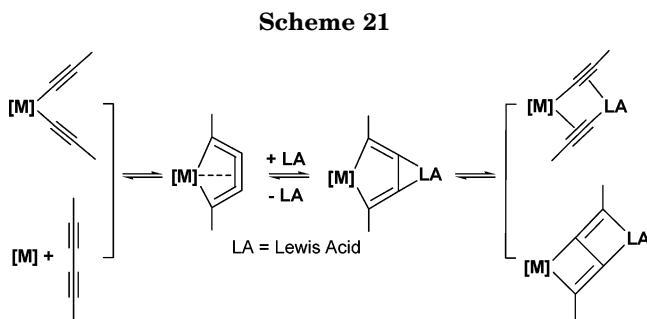
Scheme 19



The latter was stabilized by reaction with *i*-Bu<sub>2</sub>AlH to give the heterobimetallic ZrAl complex. In the case of **6** (R = Ph) two complexes were isolated after a stepwise reaction. A heterobimetallic ZrAl complex was formed first by interaction with *i*-Bu<sub>2</sub>AlH and elimination of *i*-Bu<sub>3</sub>Al. This complex added a further 1 equiv of *i*-Bu<sub>2</sub>AlH to form a trinuclear heterobimetallic ZrAl<sub>2</sub> complex (Scheme 20).



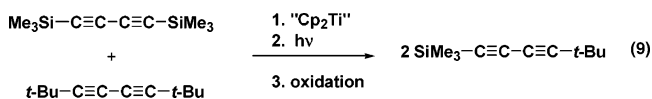
**Coupling and Cleavage Reactions.** When all these results are compiled, a general reaction scheme can be deduced, which is capable of explaining both the *cleavage of* and the *coupling to* 1,3-butadiynes (Scheme 21).



According to this, cleavage and coupling proceed via metallacyclopentadienes which interact with transition-metal complex fragments or Lewis acids (LA). There occurs *intermolecular* coordination instead of *intramolec-*

*ular* coordination of the central double bond of the cyclo-cumulene. These intermediates rearrange to afford products with cleavage or retention of the C<sub>4</sub> chains. The individual energy levels of these complexes as well as of the intermediates have been determined by calculations, and the results obtained confirm the relative thermodynamic stabilities which were observed experimentally.<sup>6c</sup>

**Photocatalytic C–C Single-Bond Metathesis.** By cleavage of two 1,3-butadiynes that contained different substituents in combination with a subsequent alternating recombination of the acetylide fragments, C–C single-bond metathesis was realized.<sup>16</sup> When mixtures of the butadiynes *t*-BuC≡CC≡C-*t*-Bu and Me<sub>3</sub>SiC≡CC≡CSiMe<sub>3</sub> were treated with 4 equiv of Cp<sub>2</sub>Ti(η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>-SiMe<sub>3</sub>) as a source of “Cp<sub>2</sub>Ti” and irradiated, *t*-BuC≡CC≡CSiMe<sub>3</sub> was detected after oxidative workup, in addition to the starting diynes (eq 9). This first titanoc-



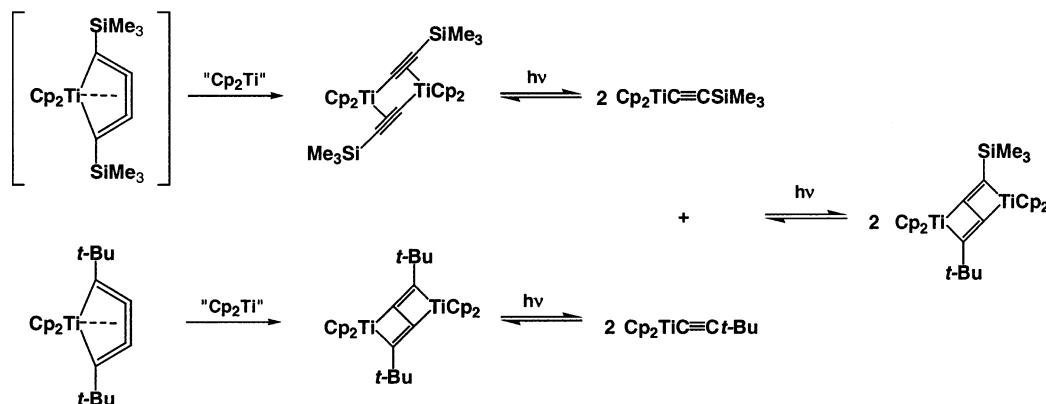
cene-mediated, photocatalyzed C–C single-bond metathesis in homogeneous solution did not proceed without titanocene or without irradiation. This metathesis cannot be conducted with only catalytic amounts of Cp<sub>2</sub>Ti, because an excess of the diyne favored coupling reactions to titanacyclopentadienes.

The suggested reaction course is shown in Scheme 22. The titanocene reacts with *t*-BuC≡CC≡C-*t*-Bu to form the titanacyclopentadiene (“cis” butadiyne complex), which interacts with further titanocene to give the binuclear “trans” butadiyne complex with an intact C<sub>4</sub> backbone. Me<sub>3</sub>SiC≡CC≡CSiMe<sub>3</sub> also forms the titanacyclopentadiene in situ, but this undergoes cleavage to form the σ,π-alkynyl-bridged complex (Scheme 12). Both complexes are cleaved under the reaction conditions, giving the unstable, monomeric Ti(III) acetylides [Cp<sub>2</sub>Ti(σ-C≡C-*t*-Bu)] and [Cp<sub>2</sub>Ti(σ-C≡CSiMe<sub>3</sub>)], which homo- or heterodimerized, producing the starting complexes or the binuclear metathesis product, respectively.


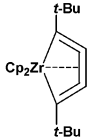

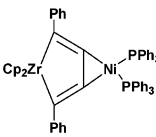
### Metallacyclopentynes

**Synthesis and Reactions.** Maercker et al. were the first to discuss a 1-titanacyclopent-3-yne as an alternative bonding description to the butatriene complex Cp<sub>2</sub>Ti(η<sup>2</sup>-Me<sub>2</sub>C=C=C=CMe<sub>2</sub>). This was assumed as an intermediate in the reaction of Me<sub>2</sub>C=C=C=CMe<sub>2</sub> and “Cp<sub>2</sub>Ti”.<sup>7c</sup> The first 1-zirconacyclopent-3-yne was reported by

**Scheme 22**

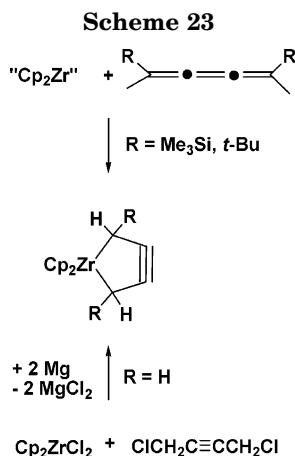


**Table 3. Comparison of Structural Data of Five-Membered Zirconacycles<sup>a</sup>**

Compounds				
References	Calculated [6h]	1 [9a]	[7f]	[9m]
Bond distances [Å]				
C1C2	CH <sub>2</sub> -C 1.509	1.28(1)	1.406(4)	1.322(5)
C3C4		1.29(1)	1.408(5)	1.331(5)
C2C3	C≡C 1.226	1.31(1)	1.237(5)	1.410(5)
ZrC1	CH <sub>2</sub> -CH <sub>2</sub> 1.590	2.357(5)	2.415(3)	2.238(4)
ZrC4	No	2.307(5)	2.428(3)	2.223(4)
ZrC2	No	2.303(5)	2.314 (3)	2.390(3)
ZrC3	No	2.306(5)	2.320(3)	2.379(3)
Angles [°]				
ZrC1C2	CH <sub>2</sub> -CH <sub>2</sub> -C 98.82	71.7(3)	Not given	79.8(2)
ZrC4C3		73.7(3)	Not given	79.7(2)
C1C2C3	CH <sub>2</sub> -C≡C 115.87	150.0(5)	151.5(3)	139.4(3)
C2C3C4		147.2(5)	151.3(3)	139.8(4)

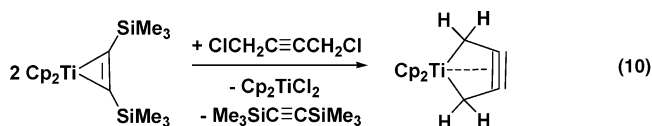
<sup>a</sup> Numbering of the C atoms refers to the central four C atoms of the butadiyne: C1 = C<sub>α</sub>, C2 = C<sub>β</sub>, C4 = C<sub>α'</sub>, C3 = C<sub>β'</sub>.

Suzuki and co-workers.<sup>7a,b</sup> Their synthesis employed the reaction of a zirconocene "Cp<sub>2</sub>Zr" source and 1,4-disubstituted (*Z*)-butatrienes RHC=C=C=CHR,<sup>7a</sup> either existing as such or generated by reaction of Cp<sub>2</sub>ZrCl<sub>2</sub> and 1,4-dichlorobut-2-yne with Mg.<sup>7b</sup> The 1-zirconacyclopent-3-yne thus produced was claimed to be the first "unsubstituted" metallacyclopentyne (Scheme 23).



The first 1-titana-cyclopent-3-yne was obtained by the reaction of 2 equiv of the titanocene source Cp<sub>2</sub>Ti(η<sup>2</sup>-

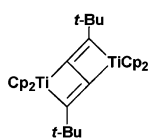

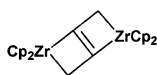
Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) with 1,4-dichlorobut-3-yne, in which one "Cp<sub>2</sub>Ti" reacts with the latter to produce Cp<sub>2</sub>TiCl<sub>2</sub> and H<sub>2</sub>C=C=C=CH<sub>2</sub> and the second complexes the butatriene thus formed, giving the titanacycle (eq 10).<sup>5h,7d</sup>



Suzuki and co-workers very recently investigated the structures of the unsubstituted 1-metallacyclopent-3-yne of titanium<sup>7e</sup> and zirconium.<sup>7f</sup> For hafnium the analogous complex with Me<sub>3</sub>Si substituents also was reported.<sup>7e</sup> Selected data of the molecular structures of the titana- and zirconacyclopentyne are compared to those of the calculated cyclopentyne and the corresponding five-membered metallacyclocumulenes (Tables 2 and 3). The triple bonds in the metallacyclopentyne (Ti, 1.248(4) Å; Zr, 1.237(5) Å) correspond very well to the calculated 1.226 Å in the metal-free cyclopentyne and are shorter compared to the central double bonds in the given metallacyclocumulene examples (Ti, 1.339-1.3) Å; Zr, 1.31(1) Å).

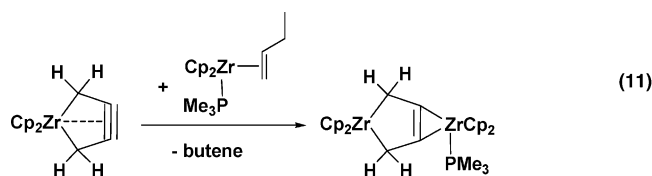
**1,3-Butadiynes and 1,2,3-Butatrienes as Bridging Ligands.** Metallacyclocumulenes and metallacy-

**Table 4. Comparison of Structural Data of Bridging “ $\mu$ -Trans” Butadiyne and Butatriene Complexes<sup>a</sup>**

Compounds			
References	[9t]	[7d]	[7f]
Bond distances [Å]			
C1C2	1.325(5)	1.443(4)	1.504(8)
C2C3	1.494(6)	1.325(5)	1.38(1)
MC1	2.093(4)	2.167(3)	2.230(7)
MC2	2.310(3)	2.268(3)	2.399(6)
MC3	2.142(3)	2.152(3)	2.196(6)
Angles [°]			
MC1C2	82.0	74.9(2)	77.3(3)
C1C2C3	128.2(4)	135.1(3)	129.6(7)

<sup>a</sup> Numbering of the C atoms refers to the central four C atoms of the butadiyne and butatriene.

cyclopent-3-yne coordinate with their unsaturated bonds to other metals to form binuclear complexes (Tables 2 and 3).<sup>5,7b</sup> Suzuki pointed out that the unsubstituted 1-zirconacyclopent-3-yne forms with “Cp<sub>2</sub>Zr(PMe<sub>3</sub>)” a cycloalkyne complex, containing a planar C<sub>4</sub> unit between the metals, described as a “flat” 1-zirconacyclopent-3-ene (eq 11).<sup>7b</sup>



Very recently also a complex of the unsubstituted 1-zirconacyclopent-3-yne with “Ni(PCy<sub>3</sub>)<sub>2</sub>” was obtained in our group.<sup>7g</sup> This also contains a C<sub>4</sub> unit between the metals. The 1-zirconacyclopent-3-ene unit in this complex is not planar, but the triple bond is elongated, as expected for Ni(0) alkyne complexes (1-zirconacyclopent-3-yne, 1.237(5) Å; its complex with Ni(PCy<sub>3</sub>)<sub>2</sub>, 1.294(9) Å).<sup>7g</sup>

As shown in eq 6, a similar reaction was found earlier in the complexation of 1-metallacyclopenta-2,3,4-trienes with “Ni(PPh<sub>3</sub>)<sub>2</sub>” in which cyclopentatriene complexes were formed, also with planar C<sub>4</sub> units between the metals.<sup>9m,n</sup> Both groups of compounds represent binuclear complexes with either “cis” butatriene or “cis” butadiyne bridging ligands (by complexation of the central triple or double bond). Metallacyclopentynes form metallacyclopentene complexes, and metallacyclopentatrienes yield metallacyclopentadienes. For the metallacyclopenta-

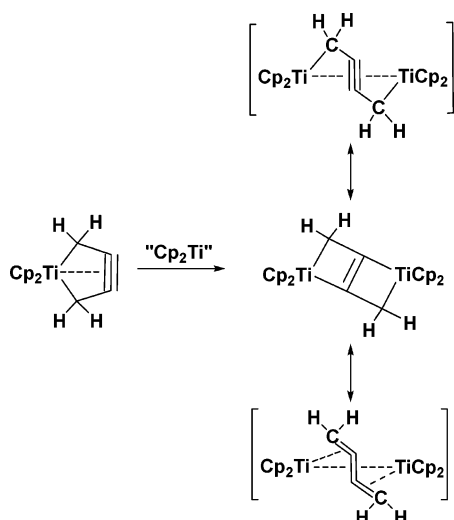
trienes, in addition to this complexation of the central double bond (eq 6), complexation of the two other double bonds also can occur: in this case metallacyclopentynes form metallacyclopentynes (see below in Scheme 26). Additionally, two “titanocenes” and diverse butadiynes yield binuclear complexes with intact C<sub>4</sub> units between the two metal centers (Scheme 12).<sup>5</sup> The former cis-complexed diynes of the metallacyclocumulenes are transformed to “zigzag-butadiene ligands” or  $\mu$ - $\eta$ (1-3): $\eta$ (2-4)-*trans,trans*-tetrahydrobutadiene moieties between two metallocene cores. This bond type is not known for M = Zr, although theoretical calculations predict its existence in the case of certain substituents.<sup>6b</sup>

The 1-titanacyclopent-3-yne mentioned above reacts with the titanocene source Cp<sub>2</sub>Ti( $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>SiMe<sub>3</sub>) with elimination of the alkyne to give a similar binuclear complex (Scheme 24).<sup>7d</sup> Its structure is represented in terms of resonance contributions of a butynediyl-bridged  $\sigma$ -propargylic complex, a butatriene-bridged  $\pi$  complex, and a  $\mu$ -*trans*-butatriene complex, but it is best described as a dititanabicyclo(2,5-dititanabicyclo[2.2.0]hex-1(4)-ene)<sup>7d</sup> in analogy to  $\mu$ -*trans*-butadiyne complexes, formed by analogous titanocene complexation of 1-titanacyclopenta-2,3,4-trienes (five-membered titana-

(15) (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 5188. (b) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 4160.

(16) Pulst, S.; Kirchbauer, F. G.; Heller, B.; Baumann, W.; Rosenthal, U. *Angew. Chem.* **1998**, *110*, 2029; *Angew. Chem., Int. Ed.* **1998**, *37*, 1915.

Scheme 24



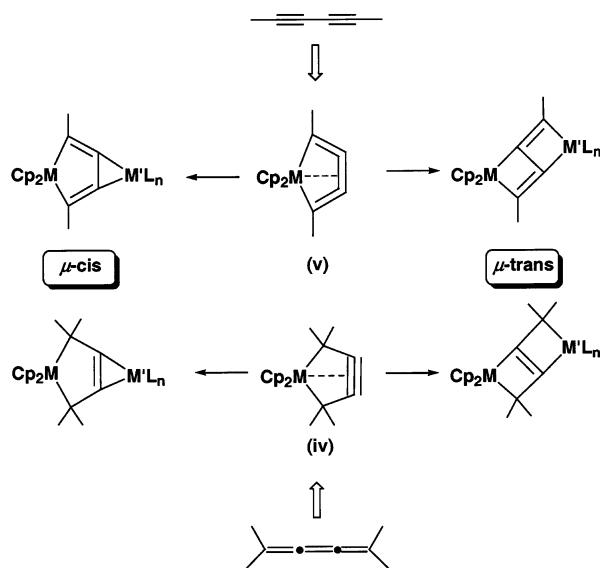
cyclocumulenes). The complex, formed from 1-titanacyclopent-3-yne and titanocene, is not a  $\sigma$ -propargyl or a  $\pi$ -allenyl complex<sup>17a,b</sup> and also is different from the “bridged allylic” structures found in ( $\mu$ -butatriene)bis(tricarbonyliron) complexes<sup>17c</sup> or substituted butadiene dianion dilithium<sup>7c</sup> and  $\mu$ -butyne-1,4-diyl structures<sup>17d</sup> as well as  $\mu$ -butadiyne complexes with  $\mu$ -( $\eta^2$ : $\eta^2$ )-(PhC=C=C=C=Ph) units.<sup>17e</sup> Very recently Suzuki obtained the analogous dinuclear zirconocene complex.<sup>7f</sup>

Structure and bonding of the dititana bicyclic complex (formed by cis complexation of two titanocene units with butatriene) were studied by DFT calculations (B3LYP/LANL2DZ). The calculated geometrical parameters were in close agreement with the experimentally found structure.<sup>7d</sup> The bonding is best described by treating the bridging ligand as a formally  $[\text{H}_2\text{CCCCH}_2]^{4-}$  species and titanium as Ti(IV). The central  $\pi$  bond perpendicular to the  $\text{TiC}_4\text{Ti}$  plane does not interact substantially with the metals. The remaining eight valence electrons of the bridging ligand occupy four in-plane delocalized orbitals resulting from the interaction with the “ $\text{Cp}_2\text{Ti}$ ” fragment orbitals. The bonding is very similar to that in the  $\mu$ -*trans*-butadiyne complex  $[\text{Cp}_2\text{Ti}]_2[\mu\text{-}\eta^2(1,3):\eta^2(2,4)\text{-RC}_2\text{C}_2\text{R}]$ , except that it has an ethylenic  $\pi$  bond in place of a *trans*-butadiene of the butadiyne complex.

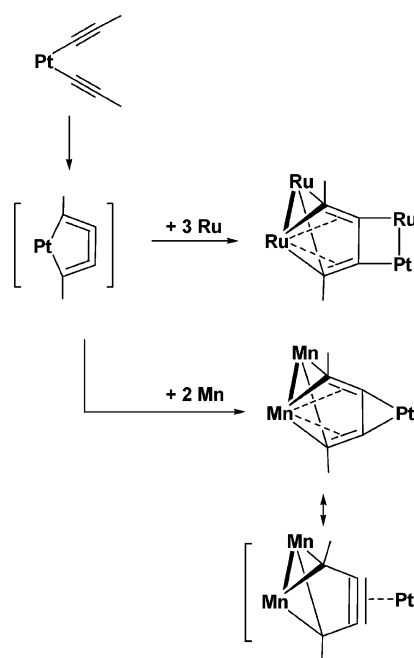
In summary, with metallacyclocumulenes and metallacyclopentynes (both as cis complexes) as starting materials, very similar bridging cis and trans complexes were obtained (Scheme 25, Tables 2–4).

Additionally, in the special case of cluster chemistry<sup>1g,h</sup> complexes with more than one metal of five-membered metallacyclocumulenes exist.<sup>14j–l</sup> Bruce et al. described a tetranuclear ruthenium cluster which contains  $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$  as a 2,5-diphenylruthenacyclopentadiene, the 3,4-substituents of which are supplied by an  $\text{Ru}_2(\text{CO})_8$  fragment.<sup>14j</sup> Yamazaki and co-workers obtained and discussed (starting from platinum acetylides) some

Scheme 25



Scheme 26

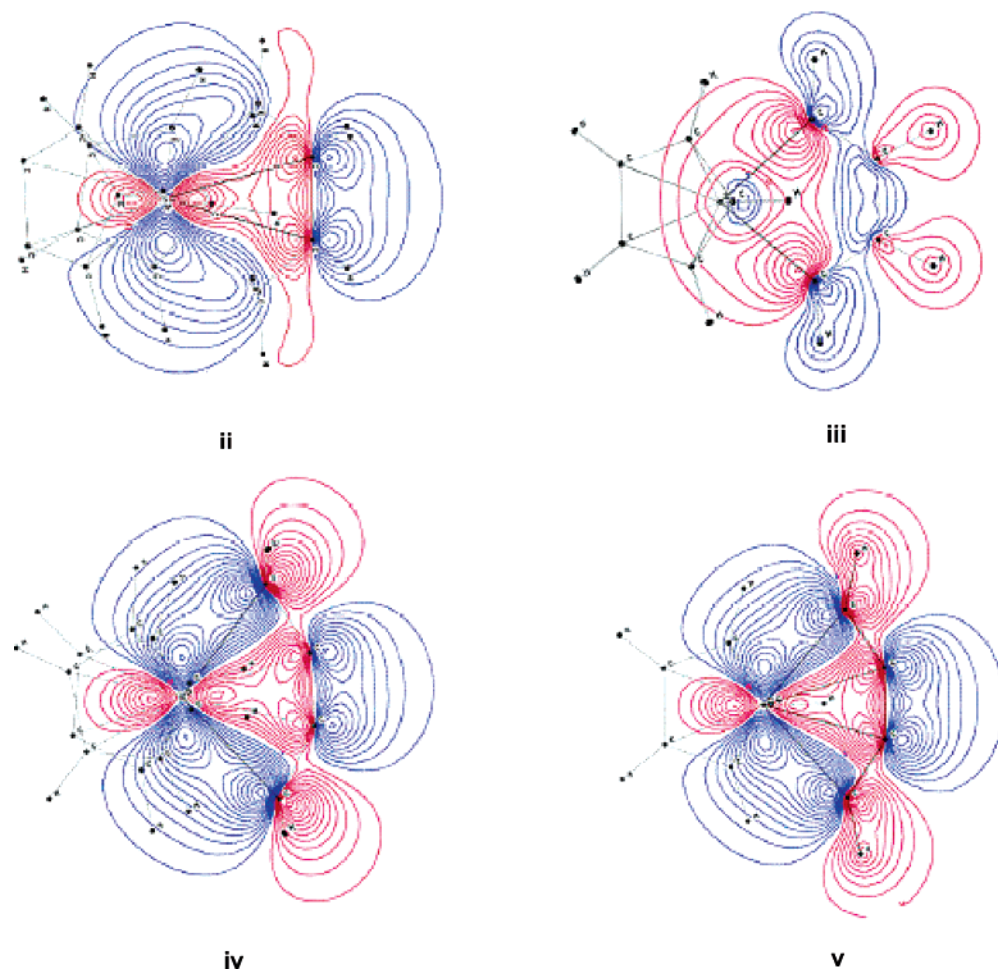


similar examples of metallacyclocumulene complexes with two metals, complexed at the central double bond<sup>14k,l</sup> (Scheme 26). Interestingly, the latter isomer<sup>14l</sup> differs from the aforementioned product of 2,3-complexation of the central double bond (eq 6) of a metallacyclocumulene by Ni(0) complexes. It corresponds more closely to Suzuki's products of 1,2,3,4-complexation of open butatrienes with the formation of metallacyclopentynes (Scheme 23). These complexes give an impression of the similarities of *metallacyclopentatrienes* and *metallacyclopentynes*.

### Comparison of Metallacyclocumulenes and 1-Metallacyclopent-3-yne

**General Considerations.** To understand the complicated bonding situation and the reactivity of the five-membered metallacyclocumulenes and metallacyclopent-3-yne, it is useful to consider it from the recently

(17) (a) Blosser, P. W.; Galucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994. (b) Blosser, P. W.; Galucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2000**, *597*, 125. (c) Gerlach, J. N.; Wing, R. M.; Ellgen, P. C. *Inorg. Chem.* **1976**, *15*, 2959. (d) Matsuo, T.; Tanaka, M.; Sekiguchi, A. *Chem. Commun.* **2001**, 503 and references therein. (e) Wang, Y.; Wang, H.; Wang, H.-S.; Chan, Z.; Xie, J. *J. Organomet. Chem.* **2003**, *683*, 39.



**Figure 3.** Contour plots of the MO's corresponding to the interaction of the metal and C2–C3 for metallacyclopentenes (**ii**), metallacyclopentadienes (**iii**), metallacyclopentynes (**iv**), and metallacyclopentatrienes (**v**).

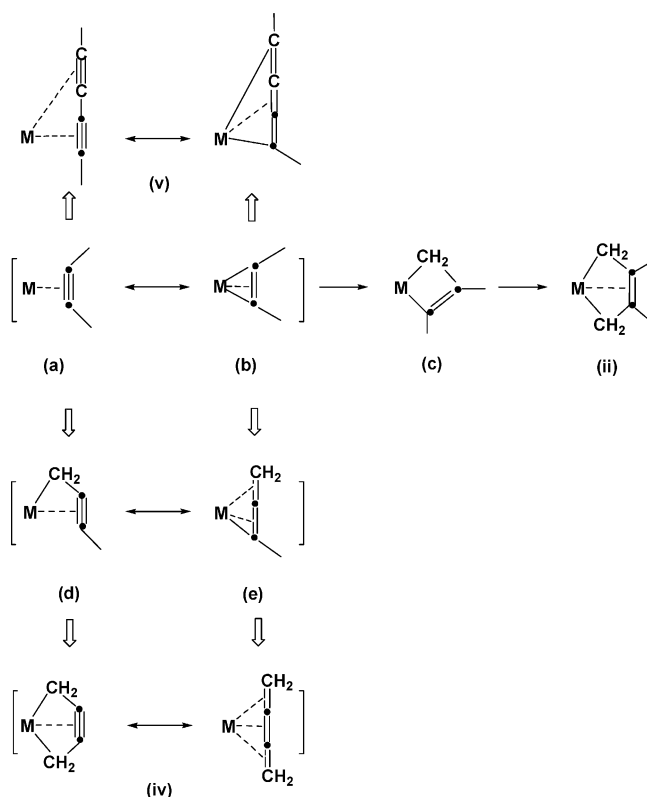
described complexation of simple embedded building blocks (Scheme 27).<sup>5h</sup> The graphical presentation in Scheme 27 should show stepwise the genesis and the relationship of the metallacyclocumulenes and the metallacyclopentynes to similar complexes. To point this out, the resonance hybrids are drawn here in an unusual form. Nevertheless, it is clear that they are different only in electronic configuration; there is no movement of nuclei (as shown in Scheme 1). The interaction of an alkyne with the electronically and coordinatively unsaturated titanocene or zirconocene center can be described by resonance structures of a metal(II) 2e  $\pi$ -complex (**a**) or metal(IV) 1,2-dianionic metallacyclopentene (**b**), for which an additional interaction of the double bond with formation of a 4e metallacyclopentene  $\pi$  complex was often discussed.<sup>18a</sup> Modification of **a** and **b** allows a formal approach to the metallacyclopentynes **iv** and metallacyclocumulenes **v** under discussion. The insertion of methylene groups  $\text{CH}_2^-$  into **a** gives stepwise, via metallacyclobutenes **c**,<sup>18b,c</sup> the metallacyclopentenes **ii**.<sup>8b-d</sup> If one substituent in **a** or **b** represents the (anionic) methylene group  $\text{CH}_2^-$ , the 1-metallacyclo-3-pentynes or  $\pi$ -buta-1,2,3-triene structures **iv**<sup>7</sup> are formed via  $\sigma$ -propargyl (**d**) or

$\pi$ -allenyl complexes (**e**).<sup>17a,b</sup> In an analogous formal consideration 1-metallacyclopenta-2,3,4-trienes or  $\pi$ -1,3-butadiyne complexes (**v**)<sup>5,6,9</sup> result if one of the substituents in **a** or **b** represents the acetylide  $-\text{C}\equiv\text{C}$ . The known  $\sigma$  and  $\pi$  interactions in metallacyclopentene, alkyne, propargyl, or allenyl complexes offer examples to understand the analogous bonding situation in **iv** and **v** as resonance structures of 1-metallacyclopenta-2,3,4-trienes and bis( $\pi$ -butadiyne) complexes and 1-zirconacyclopent-3-yne or bis( $\pi$ -butatriene) complexes.

**Calculations.** The interesting bonding situation of the unusual five-membered metallacycles **iv** and **v** prompted theoretical groups to calculate and to compare these compounds. Jemmis and co-workers were the first in this field, carrying out calculations on the metallacyclocumulenes.<sup>6b-e,g</sup> The comparison of both metallacycles was done also by Lin et al., who, on the basis of detailed electronic structure studies of the substituted complexes  $\text{Cp}_2\text{Zr}(\eta^4\text{-RHC}_4\text{HR})$  (**iv**;  $\text{R} = \text{Me}_3\text{Si}$ ) suggested that the zirconocene complex is better described by resonance hybrids involving a metallacyclopentene and a butatriene complex Lewis structure.<sup>6f</sup> From isodesmic reactions the authors concluded that the cumulene complex description contributes significantly to the stability of these complexes. The metallacyclopentene as proposed by Suzuki et al. could not describe well the structural behavior and the stability of the complex. In

(18) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (c) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbough, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584.

Scheme 27



a parallel study of the corresponding  $\text{Cp}_2\text{Zr}(\eta^4\text{-RC}_4\text{R})$  (**v**;  $\text{R} = \text{Me}_3\text{Si}$ ) Lin and co-workers found that resonance hybrids of a metallacyclocumulene and a diyne complex also adequately describe its structure and stability.<sup>6f</sup>

A comparison of the structure and bonding of all the metallacycles **i–v** by Jemmis and Jiao et al. showed considerable metal– $\pi$  interactions in **ii–v** (Figure 3).<sup>6g</sup> The analysis of geometric and magnetic properties identified the presence of strong delocalization in these five-membered metallacycles, including the metallacyclopentynes **iv**. Additionally, the metallacyclopentenes **ii** and the metallacyclopentynes **iv** were found to be “neutral bishomoaromatic,” while the metallacyclocumulene **v** is “in-plane” aromatic. A comparison of the hydrogenation energies of the parent carbocycles and metallacycles showed that the strain present in cyclopentynes and cyclopentatrienes is released when the  $\text{CH}_2$  group is replaced by a “ $\text{Cp}_2\text{Ti}$ ” or “ $\text{Cp}_2\text{Zr}$ ” fragment.

## Conclusion

Following the classical organometallic chemistry of *butadienes* with the metallocenes of Erker and Nakamura, the corresponding reactions of *butadiynes* and *butatrienes* with titanocene and zirconocene fragments led to the uncommon structures of metallacyclocumulenes and metallacyclopentynes. Interesting novel stoichiometric and catalytic C–C coupling and cleavage reactions of these compounds were found. Theoretical studies have shown that the description of these molecules is much more complicated by the influence of the metals, interacting with the unsaturated bonds in the ring. This essential element for stabilization on one hand leads to complicated interactions in the ring system on the other, which makes a simple description as cyclocumulenes and cyclopentynes impossible. Some theoretical results suggest a mesomerism of metallacycles and  $\pi$  complexes of the diynes and trienes, whereas examples of chemical reactions show an isomerism and an equilibrium between  $\eta^2$  and  $\eta^4$  coordination. One can conclude from the fact that stable five-membered metallacyclocumulenes were obtained thus far only for “ $\text{Cp}_2\text{Ti}$ ” and “ $\text{Cp}_2\text{Zr}$ ” that analogous complexes should exist also for many other metals—those which can form compounds with 1,3-butadiynes in a 14e configuration.

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