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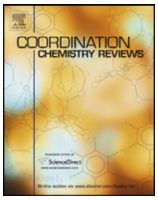

Review

Five-membered metallacycloalkynes formed from group 4 metals and [*n*]cumulene ($n = 3,5$) ligands

Noriyuki Suzuki[a,*], Daisuke Hashizume[b]

[a] *Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, Kioi-cho 7-1, Chiyoda-ku, Tokyo 102-8554, Japan*
[b] *Advanced Technology Support Division, RIKEN Advanced Science Institute, Wako, Saitama 351-0198, Japan*

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ABSTRACT

In this account [3]- and [5]cumulene complexes of group 4 metallocenes that form five-membered metallacycles are described. These complexes have a “triple bond” despite their five-membered ring structure, showing that they are regarded as 1-metallacyclopent-3-ynes. The molecular structures show their strained alkyne character. These complexes react with transition metals to form alkyne-coordinated bimetallic complexes. They also receive electrophilic attack by protons and boranes resulting in M–C bond cleavage. When a [3]cumulene couples with an alkyne on the metal, the reaction produces seven-membered metallacycloalkynes that have a strained structure showing an interaction between the “triple bond” and the metal center. Hexapentaenes, [5]cumulenes, form conjugated 1-metallacyclopent-3-ynes. The aryl-substituted [5]cumulene complex was reduced by alkali metal to give dianionic species that reacted with protons to give 1-metallacyclopent-3-ene, a cycloalkene, and with iodomethane to give 1-metallacyclopenta-2,3-diene, a cycloallene. The hexapentaene with *tert*-butyl groups reacts with zirconocene to form an η^2-π-coordinated complex in the presence of trimethylphosphine, although it gave a 1-metallacyclopent-3-yne in the absence of the phosphine. The former was transformed into the latter by addition of a phosphine, and vice versa by removing the phosphine, showing a “haptotropic” shift.

1. Introduction

Oxidative coupling of unsaturated organic compounds on transition metals results in the formation of metal-containing

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* Corresponding author. Tel.: +81 332383452; fax: +81 332383452.
E-mail address: norisuzuki@sophia.ac.jp (N. Suzuki).

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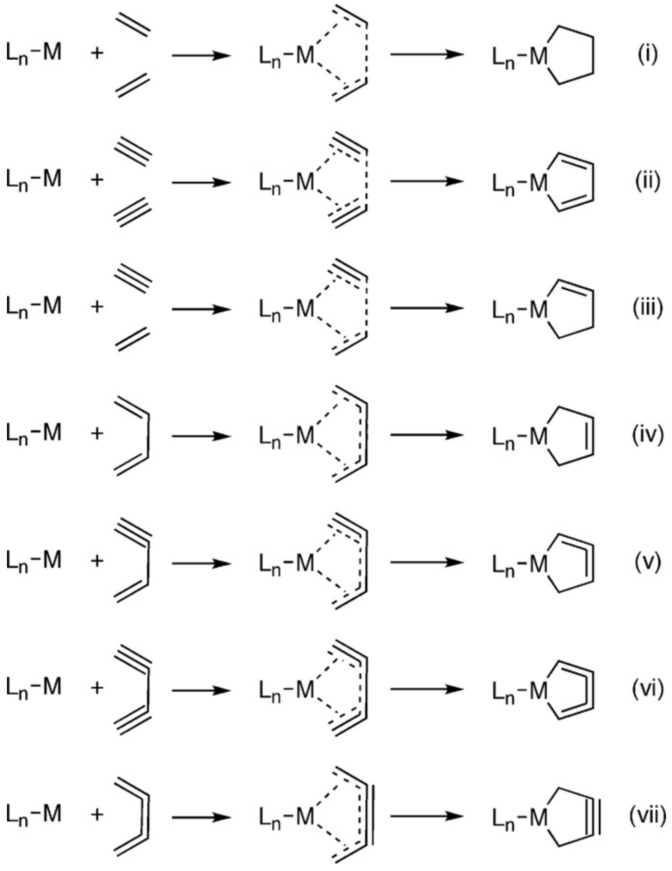
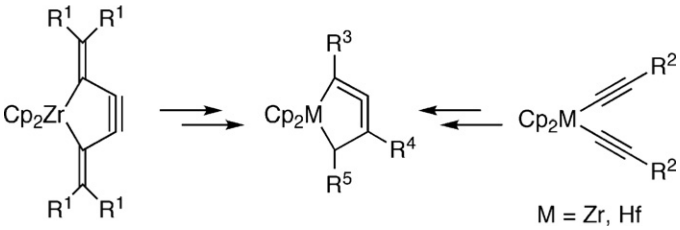
five-membered ring structures. Pauson-Khand-type reactions promoted by cobalt or rhodium complexes are typical examples that involve five-membered metallacycle formation [1–6]. Some of the alkyne trimerization reactions that give aromatic compounds are believed to proceed via five-membered metallacycles as an intermediate [7]. Not only hydrocarbons, but also hetero-atoms such as carbonyl compounds, imines, and nitriles can be involved in these reactions.

General protocols are shown in Scheme 1. Two molecules of alkenes and/or alkynes couple on the metal to form 1-metallacyclopentanes, 1-metallacyclopent-2-enes, and 1-metallacyclopenta-2,4-dienes (i–iii, Scheme 1). Oxidative coupling with early transition metals such as group 4 metallocenes has been studied extensively [8–20], as well as late transition metals. Zirconocene dichloride (Cp_2ZrCl_2), for instance, is often employed as a precursor of low-valent zirconocene, "$Cp_2Zr(II)$". Magnesium metal can reduce Cp_2ZrCl_2 in situ. The employment of "stable" Zr(II) complexes such as phosphine adducts [21] and alkyne complexes [22] is also common. Among these, the Negishi reagent, $Cp_2Zr(n\text{-}Bu)_2$, which is easily accessible from Cp_2ZrCl_2 and two equiv of *n*-butyllithium at low temperature, is effective in generating zirconocene(II) species [23]. Later, Takahashi showed that this protocol is applicable to titanocene dichloride [24], and hafnium also by Rosenthal [25]. Intramolecular coupling of conjugated compounds also makes unsaturated five-membered metallacycles. For example, 1,3-dienes make complex *s-cis* and *s-trans* complexes, the *s-cis* complexes being regarded as 1-metallacyclopent-3-enes (iv, Scheme 1). These types of complexes are known in both late transition metals [26–29] and early transition metals [30–33].

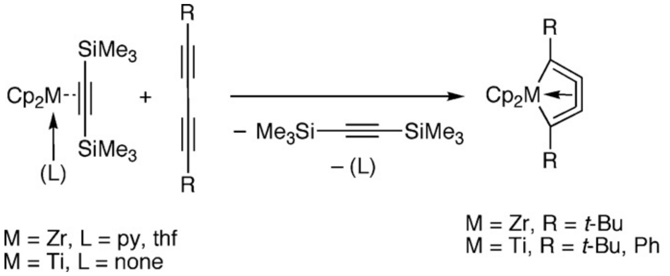
On the other hand, Eqs. (v)–(vii) are uncommon because the metallacyclic products have high ring strain and seem to be unstable. However, these three reactions have recently been achieved using group 4 metal complexes. Rosenthal reported that 1,3-diynes react with group 4 metallocenes to form five-membered [3]cumulene complexes, 1-metallacyclopenta-2,3,4-trienes (vi, Scheme 1; Eq. (1)) [34–37]. The reaction depends on the central metal, diynes, and Cp ligands. It is known that group 4 metallocenes and 1,3-diynes form bimetallic complexes (Eq. (2)) [38,39], which were originally prepared from metal-alkynyl complexes [40–43].



Scheme 1. Formation of five-membered metallacycles.



Scheme 2. 1-Metallacyclopenta-2,3-diene.



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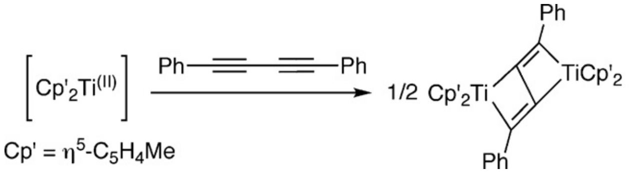
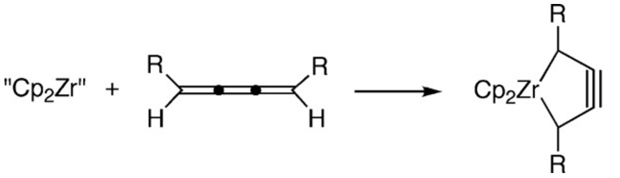


(2)

Among the many unsaturated hydrocarbons, [*n*]cumulenes ($n \geq 3$) have received much attention as ligands in coordination chemistry [44–63,64]. We recently reported that [3]cumulenes coordinates to some early transition metals to form five-membered cycloalkyne complexes, 1-metallacyclopent-3-ynes (vii, Scheme 1; Eq. (3)) [65–67].



(3)

Although one can suppose that 1,3-enynes may give cycloallenes, 1-metallacyclopenta-2,3-dienes (v, Scheme 1), this has not been achieved. Nevertheless, these complexes were recently synthesized by two groups, Erker and coworkers and our group, by different methods (Scheme 2) [68–70].

It should be noted that the reported 1-metallacyclopenta-2,3,4-triene, 1-metallacyclopent-3-yne and 1-metallacyclopenta-2,3-dienes are quite stable at room temperature. From the point of view of organic chemistry, stable five-membered alkynes, allenes and cumulenes are interesting subjects because it had been believed that these five-membered compounds would be extremely labile and therefore impossible to isolate. Indeed, hydrocarbyl cyclopentynes, five-membered cyclic alkynes, have not been isolated yet, although several preparative methods for them have been reported [71–73] as well as thiacyclopentynes [74]. Their exis-

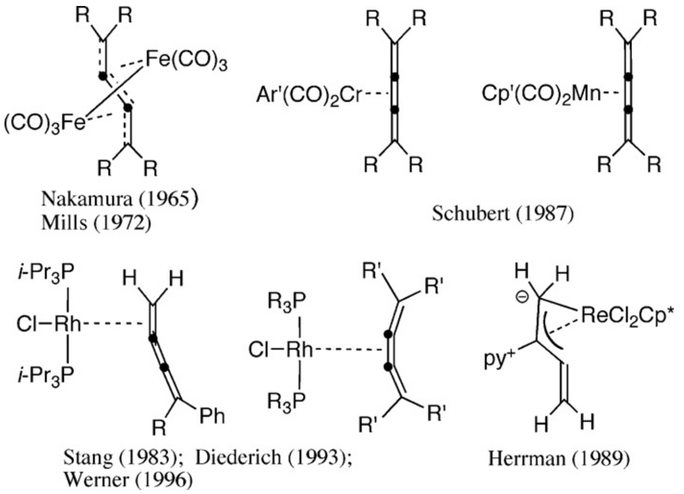


Fig. 1. Butatriene complexes of late transition metals.

tence was confirmed only spectroscopically in a matrix [75], or as trapped compounds by reactions such as [2 + 2] cycloaddition [76] or metal-complexation [77–79]. Cyclopenta-1,2-dienes, five-membered cycloallenes, have also been prepared but not isolated [80–82]. Recently small stable cycloallenes were proposed [83,84].

In this account, we describe transition metal complexes formed by coordination of [3]- and [5]cumulenes that have five-membered metallacycloalkyne structures. Their reactivity is discussed. Five-membered metallacycloallene complexes derived from [5]cumulene complexes are also shown. Because of limited space in this paper, we focus on our results plus those reported from other groups. There are many interesting examples of metal-ended cumulenes such as $M{=}[C{=}]_n{=}CRR'$ and $M{=}[C{=}]_n{=}M'$ [85], but this review will not include these compounds.

2. Syntheses of 1-metallacyclopent-3-yne complexes

2.1. Conventional [n]cumulene ($n \geq 3$) complexes

There have been several examples of [3]- and [5]cumulene complexes of transition metals [44–55]. However, no 1-metallacyclopent-3-yne complexes have been found among them. In most of these complexes, a butatriene (= [3]cumulenes) coordinates to the metal in an η^2-fashion (Fig. 1).

Butatriene complexes of group 4 metallocenes have been reported. Jones and coworkers reported that cyclohexa-1,2,3-trienes coordinated to zirconium in an η^2-π-fashion probably because of the cyclic structure of the trienes, and the complexes were stabilized as phosphine adducts (Scheme 3) [86]. Mearcker prepared a titanocene complex of 1,1,4,4-tetramethylbutatriene using 2,3-dilithio-1,3-diene. The reaction presumably formed an η^2-π-coordinated complex first, which readily rearranged via hydrogen abstraction [87].

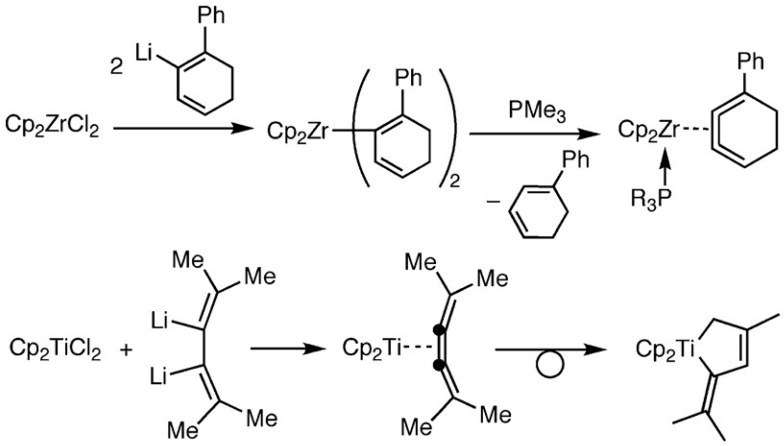
To the best of our knowledge, there have been no example of transition metal complexes of [4] and [6]cumulenes structurally characterized. There are several examples of mono- and multimetallic [5]cumulene complexes. The monometallic examples show η^2-π-coordinated structures (Fig. 2). The cumulenes coordinate to the metal by the central or the penultimate double bond in the monometallic complexes, and the coordination position is probably governed by steric demands. Irontetracarbonyl shows a variety of coordination modes such as mono-, di-, tri- and tetrametallic complexes. Cleavage of a central double bond of a hexapentaene ligand even occurs [56–63].

Nickel-catalyzed intermolecular coupling of [3]- and [5]cumulenes gives radialene compounds via nickellacycle intermediates (Scheme 4) [88–91].

2.2. Synthesis of five-membered metallacycloalkynes

We were the first to report zirconocene–butatriene complexes that showed 1-metallacyclopent-3-yne structures [65]. Low-valent zirconocene, generated from the Negishi reagent, was treated with (*Z*)-1,4-dialkyl-1,2,3-butatriene (**1**, **a**: R = $SiMe_3$, **b**: R = *t*-Bu) [92,93] to give 1-zirconacyclopent-3-yne complexes **2** in good yields as a mixture of *cis*- and *trans*-isomers (Scheme 5). In the beginning of the reaction the (*Z*)-butatrienes predominantly gave *cis*-**2**, which gradually isomerized to *trans* to reach equilibrium after 48 h at rt. Complex **2a** in solution resulted in a 36/64 *cis* and *trans* mixture, and 12/88 for **2b**. Recrystallization allowed us to isolate the *trans*-isomer as crystals. The hafnium analogue **3** is prepared similarly, using Mg/$HgCl_2$ as reducing agents [94]. It is noteworthy that the *cis*/*trans* ratio of **3** at equilibrium was 50/50. The *cis*-isomers of **2** and **3** have not been isolated so far, although they were identified by NMR spectroscopy in a solution. The titanium analogue was prepared, but the structure has not been determined [95].

Generally, it is believed that substituents adjacent to a triple bond stabilize small cycloalkynes by protecting the reactive triple bond from attack by other molecules [96–98]. For example, 3,3,7,7-tetramethylcycloheptyne (**5**, Fig. 3) was isolated [99], whereas the non-substituted cycloheptyne (C_7H_{10}) has not been obtained in a pure form [100,101]. Isolable silicon-containing cyclohexynes, 1,2,3,4-tetrasilacyclohex-5-ynes (**6**), also have alkyl groups on all silicon atoms [102,103]. Cyclooctyne (**4**) is the smallest non-substituted cycloalkyne that has been isolated [104].



Scheme 3. η^2-Butatriene complexes of group 4 metals.

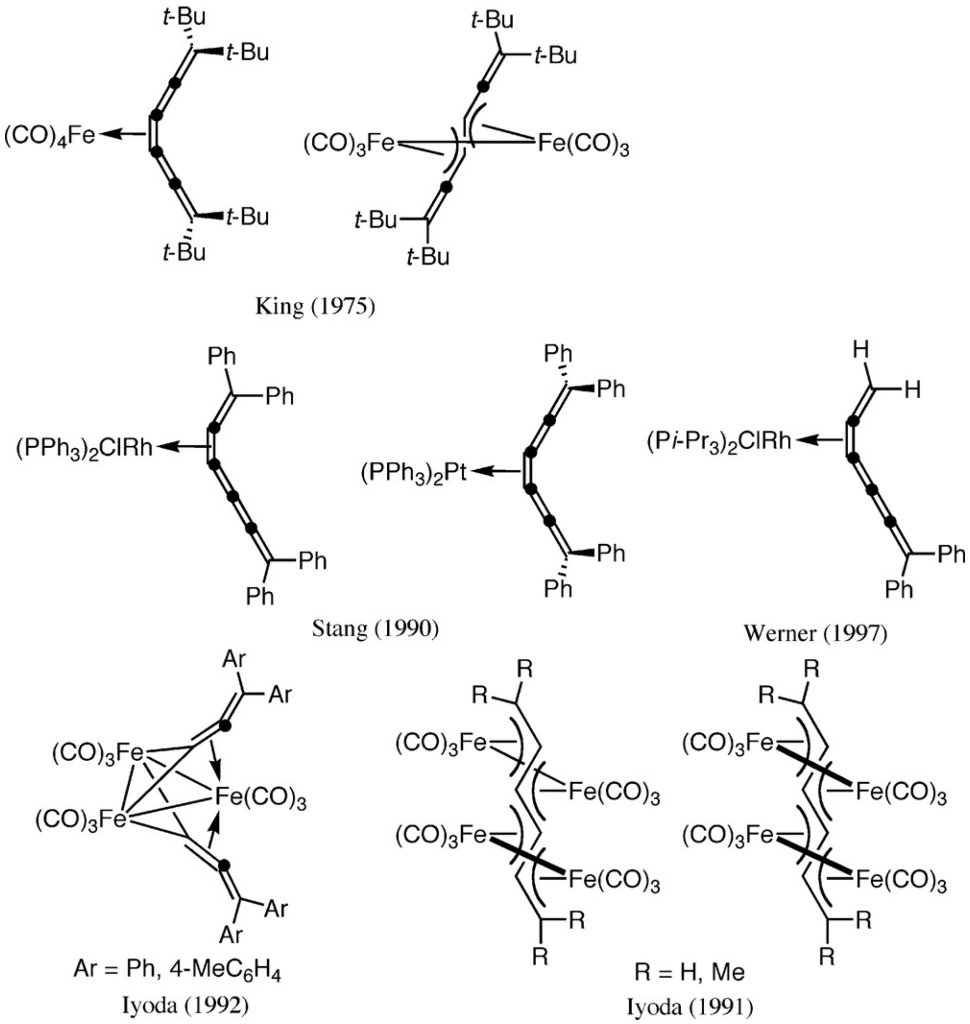
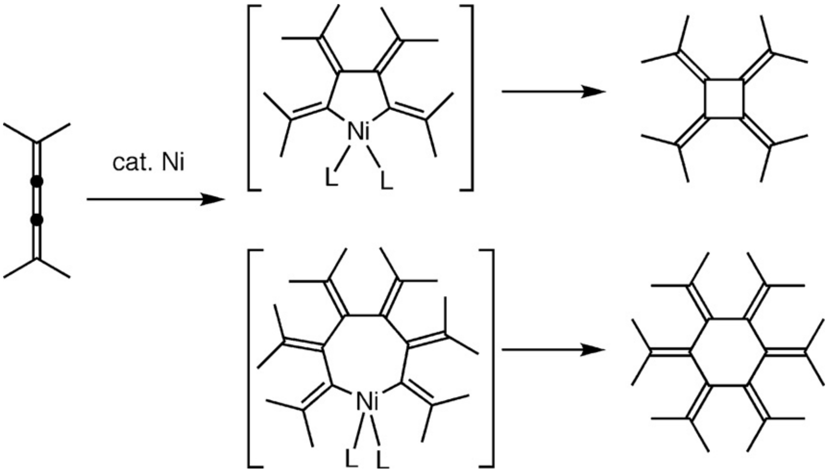


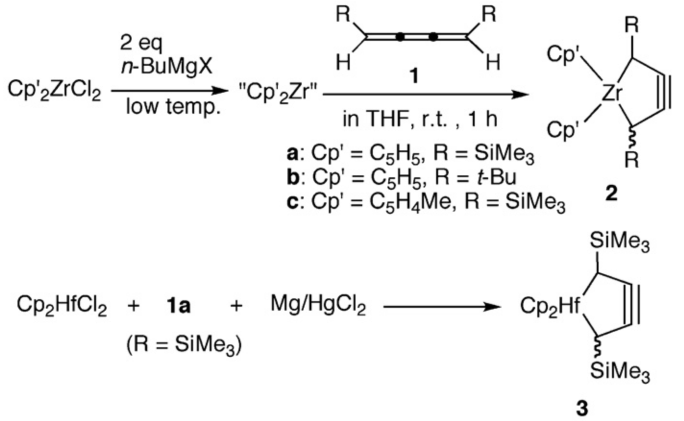
Fig. 2. Hexapentaene complexes of late transition metals.

The 1-zirconacyclopent-3-ynes **2** that we first reported had bulky substituents such as trimethylsilyl or *tert*-butyl groups at the α-position to the metal. One may think that these are responsible for stabilization of the complexes [65]. However, “non-substituted” 1-metallacyclopent-3-yne complexes **7** were found to be stable. We found a simple preparative method for **7**: a THF solution of zirconocene dichloride and 1,4-dichlorobut-2-yne was sonicated in the presence of magnesium (Scheme 6) [105]. The reaction formally gives “Cp'_2Zr” and plain butatriene in situ. These results revealed that the 1-zirconacyclopent-3-yne compounds do not owe their stability to the bulky substituents. Non-substituted 1-metallacyclopenta-2,3,4-trienes, on the other hand, have not been reported to date.

Rosenthal and coworkers first reported the 1-titanacyclopent-3-yne complex **9** using two equiv of titanocene-bis(trimethylsilyl)acetylene complex **8** as a titanocene(II) equivalent

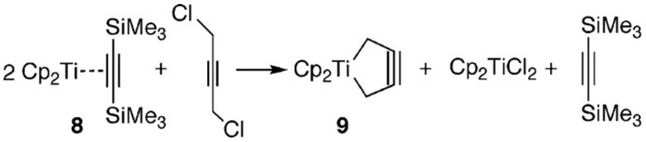


Scheme 4. Ni-catalyzed cyclooligomerization of butatrienes.



Scheme 5. Formation of 1-metallacyclopent-3-ynes.

(Eq. (4)) [106]. We reported the synthesis of **9** by a similar method to **7** and determined its molecular structure (Eq. (5)) [95].



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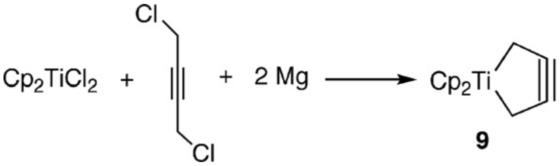
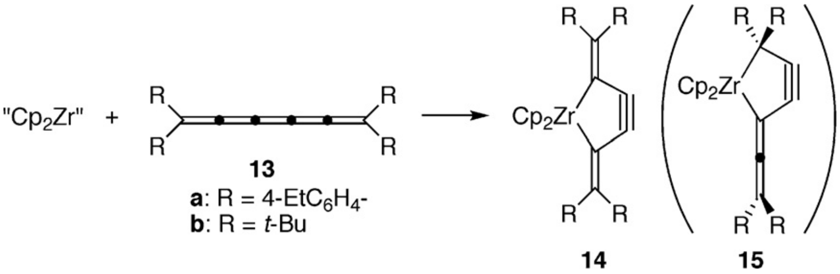


(5)

Some related complexes have been reported. Bimetallic complexes of formal 1-metalla-2,5-diazacyclopent-3-yne **10** and 1-metalla-2,5-dithiacyclopent-3-yne **11** in which the heterocycloalkyne coordinated to the other transition metals were synthesized, although the non-coordinated analogues have not been known (Fig. 4) [107,108]. Trinuclear complex **12** also showed the related structure of 1-metallacyclopent-3-yne and 1-metallacyclo-2,3,4-triene [109].

2.3. [5]Cumulene complexes

Hexapentaenes, [5]cumulenes, such as **13** also form 1-metallacyclopent-3-yne **14** by reaction with zirconocene (Eq. (6)) [68,110]. The metallacycloalkyne structure was constructed with the central three double bonds. These compounds are very stable at room temperature in crystals if they are stored under an inert atmosphere. The possible isomers **15** were not observed, probably because of steric repulsion between the bulky substituents and the Cp rings. It is of interest that interconversion between an η^2-π-coordinated complex and 1-metallacyclopent-3-yne was observed (vide infra).



(6)

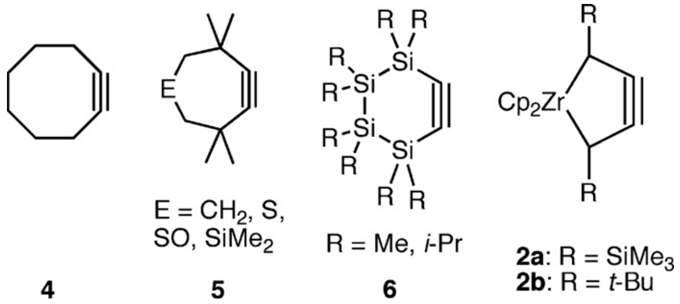


Fig. 3. Isolated cycloalkynes.

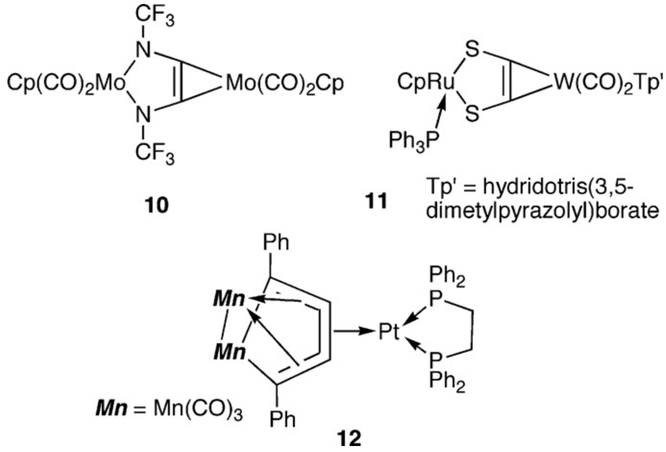


Fig. 4. Related complexes of metallacyclopentynes.

3. Molecular structures of 1-metallacyclopent-3-ynes

The molecular structure of 1-zirconacyclopent-3-yne **7a** determined by X-ray diffraction studies is compared with Rosenthal's 1-zirconacyclo-2,3,4-triene complex **16** in Fig. 5. Table 1 summarizes selected bond lengths and angles of these complexes compared with calculated values of hydrocarbyl cyclopentyne and cyclopentatriene. There are some similarities in the molecular structures between **7a** and **16**. The five-membered rings that consist of the metal and four carbon atoms have a fan shape with the metal atom at the pivot, and these five atoms are coplanar. The planes are perpendicular to the Cp(centroid)–Zr–Cp(centroid) plane. The angles C1–C2–C3 and C2–C3–C4 are about 150° in both, and these are much larger than the angles in the hydrocarbon analogues. The following are different in these two. Bond distances between the carbon atoms in the metallacycle are in the range of a double bond in **16**, which is clearly different from those in **7a**. The substituents at the metallacycle in **16** are located on the metallacycle plane, while the α-carbons have sp^3 structure in **7a**. The lengths of the C–C triple bonds in **7a** was 1.237(5) Å, which is in good correspondence to the calculated results [111,112]. In comparison with the reported larger cycloalkynes, it is similar to those

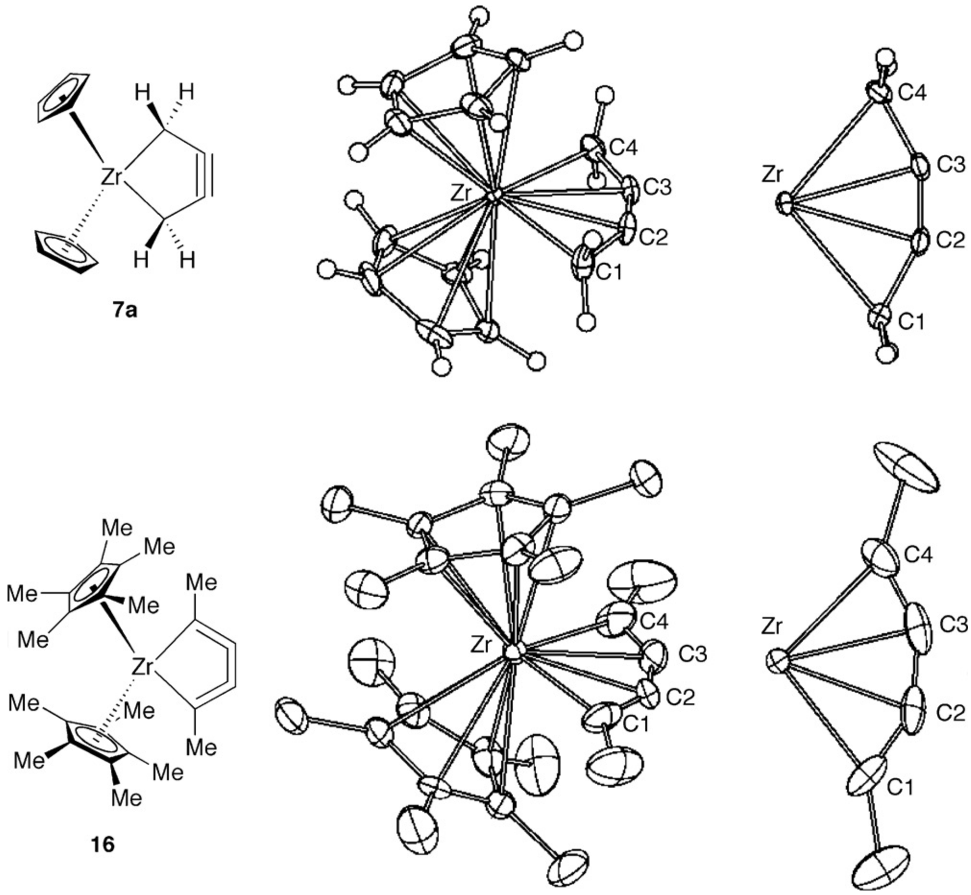
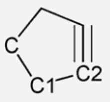
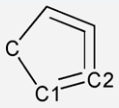


Fig. 5. The molecular structure of 1-zirconacyclopent-3-yne (**7a**) and 1-zirconacyclopenta-2,3,4-triene (**16**) complexes. The 1-zirconacycle moieties are shown. Hydrogen atoms are omitted in **16** for clarity.

of cyclononyne [113], thiacycloheptyne [114] (1.21 Å) and cyclooctyne [115] (1.23 Å). Triple bonds in small cycloalkynes are slightly longer than those in acyclic $C\equiv C$ bonds (1.167–1.197 Å) [116] due to ring strain. The $C-C\equiv C$ angles in **7a**, 151.5(3)° and 151.3(3)°, are smaller than those observed in cyclooctyne (158.5°) but larger than those in thiacycloheptyne (145.8°) [117]. The bond lengths C1–C2 and C3–C4 (1.406(4) and 1.408(5) Å) are slightly shorter than normal Csp^3–Csp^1 single bonds (1.436–1.481 Å), although they are obviously much longer than usual non-conjugated $C{=}C$ double bonds (1.280–1.347 Å). Distances Zr–C1 and Zr–C4 are 2.42 Å, while Zr–C2 and Zr–C3 are 2.32 Å. These are slightly longer than those observed in typical Zr-Csp^3 σ-bonds (e.g., 2.28 Å in Cp_2ZrMe_2) [118], but of course much longer than the C–C single bonds in cyclopentyne. The results show that the ligand coordinates to the metal in an obviously different fashion from known η^2-butatriene π-complexes.

Table 1
Bond lengths (Å) and angles (°) of five-membered triene and alkyne.

	7a	 (calculated)	**16**[a]	 (calculated)
Zr–C1	2.428(3)	C–C1 1.573	2.325	C–C1 1.576
Zr–C2	2.320(3)		2.307	
Zr–C3	2.314(3)		2.308	
Zr–C4	2.415(3)		2.335	
C1–C2	1.408(5)	C1–C2 1.472	1.285	$C1{=}C2$ 1.335
C2–C3	1.237(5)	$C2\equiv C2$ 1.271	1.312	$C2{=}C2$ 1.312
C3–C4	1.406(4)		1.283	
C1–C2–C3	151.3(3)	$C1-C2\equiv C2$ 115.4	148.2	$C1{=}C2{=}C2$ 116.37
C2–C3–C4	151.5(3)		148.5	
C1–Zr–C4	99.9(1)	C1–C–C1 108.4	97.3	
Zr–C1–C2	68.6(2)	C–C1–C2 100.2	73.1	$C-C1{=}C2$ 101.20
Zr–C4–C3	68.8(2)		72.8	
Refs.	[119]	[120]	[121]	[122]

[a] Average values of two crystallographically independent molecules.

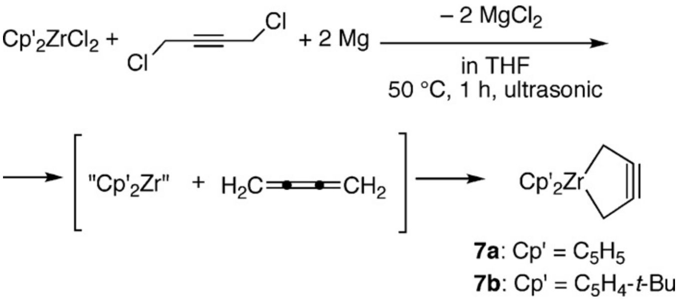
Table 2
Selected bond lengths and angles for 1-metallacyclopent-3-yne complexes.

Complexes Metals	**7a** Zr	**7b** Zr	**2a** Zr	**2c** Zr	**9** Ti	**3** Hf	**14a** Zr	**14b** Zr
C1–C2	1.406(4)	1.418(3)	1.415(7)	1.412(4)	1.393(3)	1.403(7)	1.390(2)	1.390(3)
C2–C3	1.237(5)	1.237(3)	1.206(7)	1.231(4)	1.248(4)[a]	1.229(7)	1.263(2)	1.258(2)
C3–C4	1.408(5)	1.417(3)	1.400(6)	1.409(4)		1.407(7)	1.388(2)	–
M–C1	2.415(3)	2.414(2)	2.500(6)	2.452(3)	2.353(2)	2.429(5)	2.347(2)	2.393(2)
M–C2	2.314(3)	2.311(2)	2.289(5)	2.295(3)	2.202(2)	2.276(5)	2.338(2)	2.307(2)
M–C3	2.320(3)	2.305(2)	2.289(6)	2.294(3)		2.276(5)	2.336(2)	–
M–C4	2.428(3)	2.433(2)	2.504(4)	2.466(3)		2.431(5)	2.341(2)	–
C1–C2–C3	151.5(3)	150.8(2)	155.9(7)	153.3(3)	151.7(1)[b]	153.0(5)	147.3(2)	150.3(2)
C2–C3–C4	151.3(3)	152.3(2)	156.2(6)	154.1(3)		153.1(5)	147.3(2)	–
C1–M–C4	99.9(1)	100.6(1)	98.1(2)	99.7(1)	103.8(1)[c]	100.4(2)	100.4(1)	100.3(1)
M–C1–C2	68.8(2)	67.7(1)	64.8(3)	66.7(2)	66.4(1)	66.8(3)	72.4(1)	69.4(1)
M–C4–C3	68.6(2)	68.6(1)	64.8(3)	66.2(2)		66.7(3)	72.5(1)	–
Metallacycle plane to Cp(c)–M–Cp*(c)[d]	89.6(4)	89.4(1)	86.1(4)	85.4(1).	89.3(1)	86.0(2)	85.4	87.9
Σ(C1)[e]	340.8	344.9	344.2	340.1	349.6	339.4	–	–
Σ(C4)[e]	340.1	346.5	342	345.4		339.6	–	–
Refs.	[119]	[105]	[65]	[94]	[94]	[94]	[68]	[110]

[a] C2–C2*.
[b] C1–C2–C2*.
[c] C1–Ti–C1*.
[d] The angle between the metallacyclopentyne plane and the Cp(c)–M–Cp(c) plane; Cp(c): centroid of the Cp rings.
[e] The summation of the three bond angles (excluding the C–Zr bond) at C1 and C4.

Other examples of 1-metallacyclopent-3-ynes such as complexes with substituents, titanium and hafnium analogues, and the α,α′-bisalkylidene complexes derived from [5]cumulene are summarized in Table 2. The complexes with bulky substituents such as trimethylsilyl groups (*trans*-**2a**) have similar structures to **7a** except that the metallacycle plane is tilted slightly out of perpendicular to the Cp(centroid)–Zr–Cp(centroid) plane (85.4(1)°) due to steric repulsion between the trimethylsilyl groups and the Cp rings (Fig. 6). It is noteworthy that this tilt was observed also in [5]cumulene complexes **14**, although they have alkylidene substituents at the α-positions.

The hafnium complex *trans*-**3** was nearly isostructural to the zirconium analogue *trans*-**2a**. With regard to the titanium complex **9**, on the other hand, some features are noteworthy. The Ti-C bonds in the 1-titanacyclopent-3-yne are significantly shorter than the corresponding Zr–C and Hf-C bonds. The C1–C2 bond length in **9** is slightly shorter than those in the Zr and Hf complexes, whereas the C2–C2′ distance is longer than those (C2–C3) in the Zr and Hf complexes. The sum of the three bond angles (excluding the C–metal bond) at C1 and C4 is 350° for **9**, being larger than those in the Zr and Hf complexes (340–345°). This may be related to the coordination mode of butatriene in the metallacycles (vide infra). Complexes of [5]cumulene **14** show a few differences from those of [3]cumulenes in their molecular structures. Complexes **14** have longer triple bonds compared with those in [3]cumulene complexes, whereas the single bonds are slightly shorter. The distances Zr–C1 and Zr–C4



Scheme 6. Preparation of "non-substituted" 1-zirconacyclopent-3-yne.

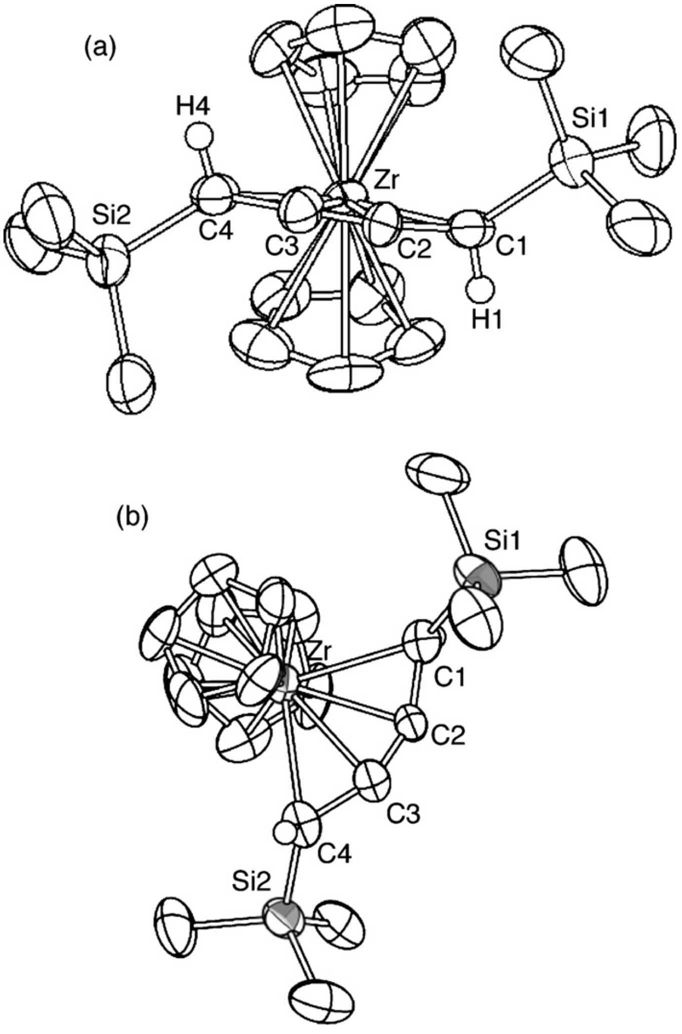


Fig. 6. Molecular structure of *trans*-**2a**; (a) front view, (b) top view.

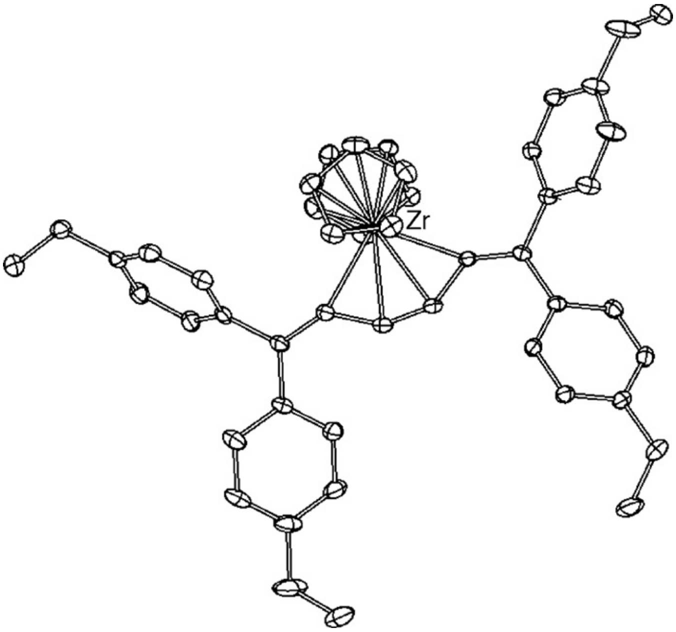


Fig. 7. The molecular structure of **14a**. Drawn with 50% probability. Hydrogen atoms are omitted for clarity.

in **14** are shorter than those in [3]cumulene complexes, while Zr–C2 and Zr–C3 are rather longer (Fig. 7).

It should be emphasized that these 1-metallacyclopent-3-yne complexes are very stable at room temperature as crystals despite their strained structures if they are stored under an inert atmosphere.

Selected chemical shifts in the ^{1}H and ^{13}C NMR spectra and coupling constants ($^1J_{CH}$) are shown in Table 3. Protons at the α-carbons were observed at 2–3 ppm showing their sp^3 character; they appeared downfield in the order Ti > Zr > Hf, while the Cp signals were in the order Ti < Zr ≈ Hf. It is known that Cp protons in the titanocene(II) and zirconocene(II) complexes of a π-coordinated alkene or alkyne appear at higher magnetic field compared with the dialkyltitanocenes(IV) and zirconocenes(IV) [123–125]. The Cp protons of 1-metallacyclopent-3-ynes were observed in the range 4.7–5.2 ppm, indicating the electron-rich character of the central metals. It is noted that Cp protons of **14** appeared slightly downfield, implying that the conjugated system decreased the electron density of the metal center. In the ^{13}C NMR spectra, chemical shifts of C2 (=C3) at the triple bond are 99–109 ppm. It has been reported that the acetylenic carbon appears at lower field as the ring strain increases [96,102]. For instance, it appears at 100–110 ppm in cycloheptynes, 91–100 ppm in cyclooctynes, 82–90 ppm in cyclononynes, and 80.9 ppm in acyclic 3-hexyne. Considering that the angles C1–C2–C3 and C2–C3–C4 are similar to those for cyclooctyne, the chemical shifts for C2 and C3 in these complexes are best attributed to a triple bond in a strained ring. In the reported zirconium-alkyne complexes, the acetylenic carbons of coordinated alkynes appear as far downfield as 170–220 ppm [126], suggesting that coordination of the triple bond is unlikely in the 1-metallacyclopent-3-yne complexes. Carbons attached to Ti metals are commonly observed at lower field compared with the corresponding Zr and Hf compounds [127–129], and the same tendency is shown here. It may be noted that the coupling constants ($^1J_{CH}$) at C1 are larger in the Ti complexes than in the corresponding Zr and Hf complexes. These NMR data are consistent with the larger contribution of η^4-π,π-coordination in the titanium complexes suggested by structural analysis.

Infrared (IR) spectroscopy of the 1-metallacyclopent-3-ynes showed weak to moderate C(C stretching bands at 2011–2018 cm^{-1} for all zirconium and hafnium complexes, while the titanium complex **9** showed absorption at 2029 cm^{-1}. These absorb at slightly lower energy than known cyclic alkynes (2100–2200 cm^{-1}). This is in a sharp contrast to Zr-alkyne complexes, which show a band in the region for a double bond (i.e., 1611 cm^{-1}) [126]. The absorption due to the triple bond of [5]cumulene complexes **14** was observed at much lower energy, such as 1888 cm^{-1} for **14a** (Raman spectroscopy) and 1912 cm^{-1} for **14b** (IR). It is consistent with longer triple bonds in these complexes (1.26 Å). Although the reason for longer triple bonds in **14** is unclear yet, it might be rationalized similarly to a longer central bond in [5]cumulenes [130–132].

4. Why is 1-zirconacyclopent-3-yne so stable? Interpretation of the bonding mode of 1-metallacyclopent-3-yne complexes

From where does the remarkable stability of these highly strained 1-metallacyclopent-3-ynes originate? Two theoretical chemistry research groups independently tried to rationalize this issue based on the refined structure by DFT calculations, just after the first synthetic work was published [65]. Jemmis and coworkers suggested that electron donation from the triple bond to the metal increases the stability of this compound; that is η^2-σ,σ + η^2-π-coordinated structure (Form **B** in Fig. 8) as well as they proposed for 1-metallacyclopenta-2,3,4-trienes [112,133]. Lin and Lam, on the other hand, proposed a contribution of a η^4-π,π-coordinated structure (Form **C**) [111]. Although both groups derived almost the same structure from their calculations, quite different results were reported. To clarify the bonding mode of the complexes, we analyzed the electron density distribution of the one of those experimentally using the accurate X-ray diffraction data, which provides valuable information on the bonding mode by observing the electron density distribution in the complex [134].

The data must be highly accurate to obtain the electron density distribution of the outer shells of the atoms in particular. Thus, we collected new diffraction data of **7b** using synchrotron radiation at the KEK PF-AR NW2 beamline although conventional X-ray diffraction measurements have already been performed. The data were analyzed using a multipole expansion method [135]. Here, the carbon atoms of the 1-zirconacyclopent-3-yne moiety are abbreviated as C(α) and C(β) for atoms at the 2- and 5-, and the 3- and 4-positions, respectively. The structural features of **7b** are essentially the same as those described in previous work (Fig. 9) [105]. The bond distances and angles in the five-membered ring are in good accordance with those from DFT calculations (Table 4) [111,112,133].

Fig. 10 shows different sections of the Laplacian maps focused on the 1-zirconacyclopent-3-yne moiety, based on the experimental electron density distribution. The map shows similar features to that of the DFT calculation of Lin and Lam, in particular, those around the metal center. The σ-coordinations of the C(α) atoms to the Zr atom are clearly observed as the valence shell charge

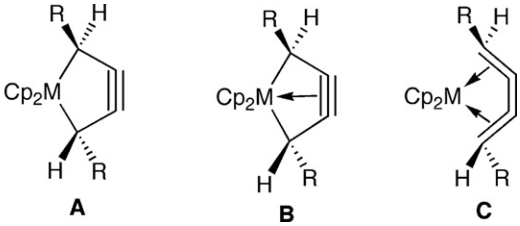
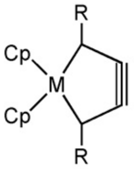
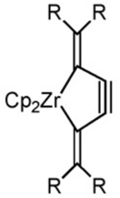


Fig. 8. The suggested bonding modes of the 1-zirconacyclopent-3-yne complex.

Table 3
Selected ^{1}H and ^{13}C NMR spectroscopic data (ppm) for 1-metallalcyclopent-3-yne complexes[a].



2a: M = Zr, R = $SiMe_3$
7a: M = Zr, R = H
9: M = Ti, R = H
3: M = Hf, R = $SiMe_3$
17: M = Ti, R = $SiMe_3$
18: M = Hf, R = H



14a: R = 4-EtC_6H_4-
14b: R = *t*-Bu

$^{1}H/^{13}C$		Ti	Zr		Hf
		cis-**17**	*cis*-**2a**		*cis*-**3**
^{1}H	C*H*	2.49	2.19		2.02
	C_5H_5	4.86, 5.03	5.00, 5.36		4.96, 5.30
^{13}C	*C*H	53.44	38.91		37.45
	C≡C	107.96	102.92		98.27
		trans-**17**	*trans*-**2a**		*trans*-**3**
^{1}H	C*H*	2.28	2.15		1.95
	C_5H_5	4.94	5.18		5.13
^{13}C	CH ($^{1}J_{CH}$)[b]	53.66 (136)	39.48 (131)		37.99 (132)
	C≡C	108.80	103.59		98.80
		9[c]	**7a**		**18**
^{1}H	CH_2	3.03	2.73		2.54[d]
	C_5H_5	4.68	4.99		5.15[d]
^{13}C	CH_2 ($^{1}J_{CH}$)[b]	51.18 (159)	38.64 (154)		nd[e]
	C≡C	106.88	102.45		nd[e]
			14a	**14b**	
^{1}H	C_5H_5		5.36	5.38	
^{13}C	*C*≡C		103.82	100.30	

[a] In C_6D_6.
[b] In Hz.
[c] Ref. [106].
[d] In THF/C_6D_6.
[e] Not detected.

concentration (VSCC) on the C(α) atoms extending towards the charge depletion regions around the Zr atom along the bond directions (Fig. 10). The distribution also implies a trace π-bonding character of the C(α)-C(β) bonds. The VSCCs on the C(α) atoms increase slightly along the Zr–C(α) bond directions, and are spread over the C(α)–C(β) bonds, rather than being localized on the C(α) atoms. These results show that a small portion of the π-electron on the C(α) atom is delocalized over the C(α)–C(β) bond in the 1-zirconacyclopent-3-yne plane. This delocalization brings about the π-bonding in the C(α)–C(β) bonds, namely the 'in-plane' π-bonding, suggesting a slight contribution of an η^4-π,π-coordination (Form **C**). In addition, as shown in Fig. 10(b), the VSCC at the center of the C(β)–C(β) bond deforms vertically to the 1-zirconacyclopent-3-yne plane. This feature of the VSCC also indicates an 'in-plane' π-delocalization of the C(β)–C(β) bond over the C(α)–C(β) bonds. The delocalization of the π-electrons over the but-2-yne-1,4-diyl ligand changes the bond distances of the ligand from those of the localized structure (Form **A**): the C(α)–C(β) bonds are shortened, and the C(β)–C(β) bond is elongated. We consider the complex to correspond to that suggested by Lin and Lam, where the complex is a resonance hybrid between the η^2-σ,σ- (Form **A**) and η^4-π,π-coordinated structures (Form **C**). We also tried to account for our results based on Form **B**. However, this structure cannot fully explain our results, in particular, the shortening of the C(α)–C(β) bonds.

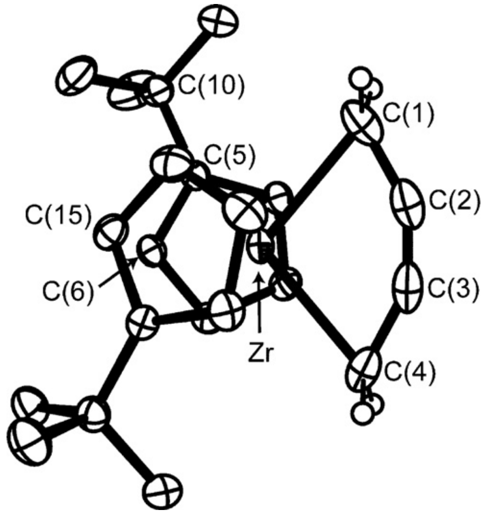


Fig. 9. The molecular structure of **7b**.

Topological analysis of the total electron density distribution evaluates the interaction between the Zr and but-2-yne-1,4-diyl

Table 4
The experimental geometric parameters of **7b**, and a comparison with values from DFT studies.

Refs.	Experimental [134]	Calculated 1 [112]	Calculated 2 [111]
Distance/Å			
Zr–C(1)	2.4193(15)	2.440	2.493
Zr–C(2)	2.3181(15)	2.330	2.328
Zr–C(3)	2.3169(15)	2.330	2.328
Zr–C(4)	2.4361(15)	2.440	2.493
C(1)–C(2)	1.409(3)	1.424	1.407
C(2)–C(3)	1.250(3)	1.259	1.250
C(3)–C(4)	1.413(3)	1.424	1.407
Angle/°			
C(1)–C(2)–C(3)	150.97(14)	151.2	153.9
C(2)–C(3)–C(4)	151.80(14)	151.2	153.9

Table 5
Topological analysis of the bond critical points in ρ.

	$\rho(\mathbf{r}_{\text{bcp}})$/e Å^{-3} [a]	$\nabla^2\rho(\mathbf{r}_{\text{bcp}})$/e Å^{-5} [b]	λ_1/e Å^{-5} [c]	λ_2/e Å^{-5} [c]	λ_3/e Å^{-5} [c]	ε [d]
Zr–C(1)	0.36	4.4	−1.3	−0.8	6.5	0.64
Zr–C(4)	0.35	4.5	−1.3	−0.8	6.6	0.68
Zr–C(6)	0.28	3.4	−1.0	−0.3	4.7	2.4
Zr–C(15)	0.28	3.4	−1.1	−0.3	4.8	2.2
C(1)–C(2)	2.09	−18.3	−13.5	−11.7	6.9	0.16
C(2)–C(3)	2.97	−40.9	−23.1	−19.8	2.0	0.17
C(3)–C(4)	2.16	−20.8	−14.4	−12.5	6.1	0.15
C(5)–C(6)	1.99	−14.9	−13.9	−11.5	10.5	0.21
C(5)–C(10)	1.77	−12.4	−11.1	−10.9	9.5	0.02

[a] $\rho(\mathbf{r}_{\text{bcp}})$ indicates the electron density at the bond critical points.
[b] $\nabla^2\rho(\mathbf{r}_{\text{bcp}})$ indicates the Laplacian of the electron density at the bond critical points.
[c] λ_i denotes the eigenvalues of the Hessian matrix of $\rho(\mathbf{r}_{\text{bcp}})$.
[d] ε is the bond ellipticity, $\varepsilon = \lambda_1/\lambda_2 - 1$.

ligand quantitatively. The bond critical points and bond paths are observed on the Zr–C(α) bond, as well as for all bonds of the ligands and the bondings of Zr-cyclopentadienes (Fig. 11). These were not found between the Zr and C(β) atoms, and the Zr and the C(β)–C(β) bond. In addition, no deformation of π-electrons on the C(β)–C(β) bond towards the Zr atom was observed (Fig. 10(b)). These results strongly support the σ-coordination of the C(α) atoms to the Zr atom without the π-donation of the C(β)–C(β) bond (Form **A**). The absence of bond critical points between the Zr and C(β) atoms and/or the C(β)–C(β) bond, and the π-electron distribution on the C(β)–C(β) bond clearly shows an absence of any interatomic interaction between them. The values of $\rho(\mathbf{r}_{\text{bcp}})$ and $\nabla^2\rho(\mathbf{r}_{\text{bcp}})$ are listed in Table 5 for the Zr–C(α), the C–C bonds of the but-2-yne-1,4-diyl ligand and some Zr–Cp′ bonds. A trace of the π-bonding component between the C(α)–C(β) bond and the Zr atom was also shown by our topological analysis. As shown in Fig. 11, the endo-curved bond paths of the Zr–C(α)bonds near the C(α) atoms clearly show the contribution of the π-coordination of the C(α)–C(β) bond to the Zr–C(α) bond. In addition, a significantly large values of ε for the Zr–C(α) bonds was observed. The contribution of the π-coordination however, must be small, because no bond paths or bond critical points were found between the Zr and C(β) atoms.

Thus we conclude that the topology of the experimental electron density distribution shows a resonance hybrid between the η^2-σ,σ- and η^4-π,π-coordinations. The major contributor is the η^2-σ,σ-coordination, while the contribution of the η^4-π,π-coordination is small. These results are in agreement with our previous studies based on spectroscopic analysis and hydrolysis reactions [65].

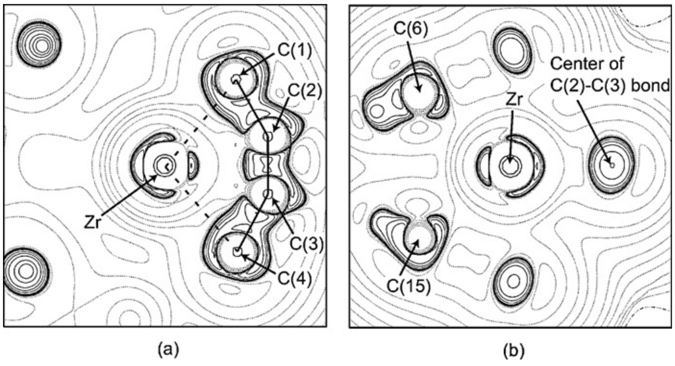


Fig. 10. Laplacian distribution plots of (a) the plane defined by the Zr, C(1), and C(4) atoms and (b) the cross section of the Zr–C(1)–C(4) plane passing through the Zr atom and the center of the C(2)–C(3) bond. The dotted contours denote positive values of $\nabla^2\rho(\mathbf{r})$, the solid lines denote negative values of $\nabla^2\rho(\mathbf{r})$, and the broken lines in (a) and (b) denote the Zr–C(α) bonds. Positive and negative contours indicate regions of local charge depletion and concentration, respectively. The contours are drawn at $\pm 2\times 10^n$, $\pm 4\times 10^n$ and $\pm 8\times 10^n$ (where $n = -2, -1, 0, 1, 2$) eÅ^{-5}.

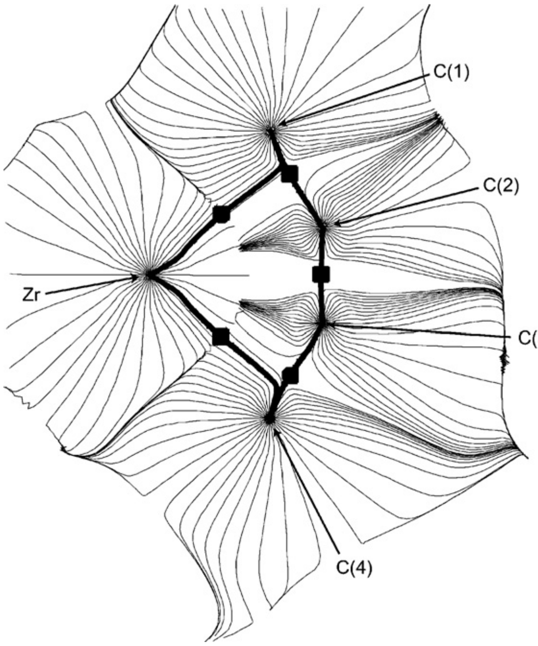


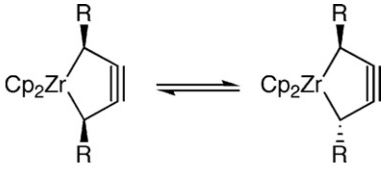
Fig. 11. Gradient trajectories (fine lines), bond paths (bold lines) and bond critical points (filled squares) in the plane defined by Zr, C(2) and C(3). The bond paths of the Zr–C(α) bonds curve inwardly with respect to the 1-zirconacyclopent-3-yne ring. These indicate that the 'in-plane' π-coordination of the C(α)–C(β) bond contributes to the Zr–C(α) bond.

5. Reactivity of 1-metallacyclopent-3-ynes

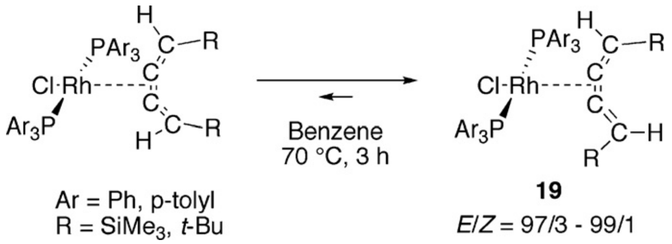
5.1. Isomerization of the cumulene ligand on transition metals

Group 4 metallocenes and (*Z*)-1,4-dialkyl butatriene forms *cis*-2,5-dialkyl-1-metallacyclopent-3-ynes that gradually isomerize to the *trans*-complexes at rt (Scheme 7) [65]. Although the mechanism of the isomerization is still vague, it might proceed via hydrogen abstraction or a radical process.

Cumulenes isomerize with a lower energy barrier, such as 30 kcal mol^{-1} for butatriene and 20 kcal mol^{-1} for hexapentaene



Scheme 7. Isomerization of 1-metallacyclopent-3-yne.



Scheme 8. Isomerization of butatrienes on Rh complexes.

[136,137]. Indeed, a trace amount of iodine catalyzes the *cis–trans* isomerization of [3]cumulenes [138,139]. Organocopper species promoted the *E*–*Z* isomerization of butatrienes [140]. We observed that isomerization of (*Z*)-**1a** to (*E*)-**1a** was catalyzed by nickellocene to give a 1:1 *cis*/*trans* mixture [141]. We prepared the rhodium complex of (*Z*)-butatrienes (*Z*)-**1a** and (*Z*)-**1b** in which the ligand coordinates to the metal in an η^2-π-fashion. Upon heating in benzene-d_6 at 70 °C for 3 h, the ligand isomerized to the (*E*)-form (Scheme 8) [142]. It is noteworthy that the *E*/*Z* ratio in the equilibrium mixture was 97/3 to 99/1. The high *E*-selectivity might be because of steric repulsion in the *Z*-complexes. 1-Metallacyclic structures, however, were not observed in these rhodium complexes (Fig. 12).

5.2. Coordination to other metals

As mentioned above, contributions of both five-membered cycloalkyne and η^4-π,π-coordinated modes are considered to rationalize the stability of [3]- and [5]cumulene complexes of group 4 metals. If it is a cycloalkyne, it may coordinate to the other metal as an unsaturated ligand. Indeed, **7a** reacted with the zirconocene-but-1-ene complex-trimethylphosphine adduct **20** to give bimetallic complex **21** as a result of ligand exchange between but-1-ene on the zirconium and **7a**. In this complex, **7a** coordinates to the other zirconium metal as an alkyne and complex **21** showed a similar structure to those of known zirconocene–cycloalkyne complexes [77,125]. The length of the coordinated triple bond (1.336(4) Å) was longer than that of **7a**. The angles around the sp-carbons (136.7(3) and 140.6(3)°) were smaller. The nickel-coordinated complex **22** was reported by Rosenthal [143]. It is noteworthy that the Ni-coordinated complex **22** showed the bent 1-zirconacyclopent-3-ene structure showing coordination of the double bond to the zirconium metal while the metallacycle was almost flat in the homobimetallic complex **21**. The cyclocumulene complexes, 1-metallacyclo-2,3,4-trienes, also form bimetallic metal-coordinated complexes **23** [144–150] (Scheme 9).

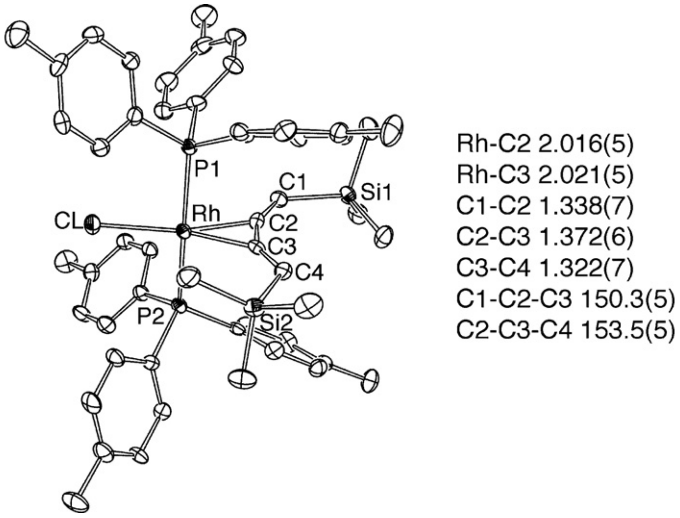
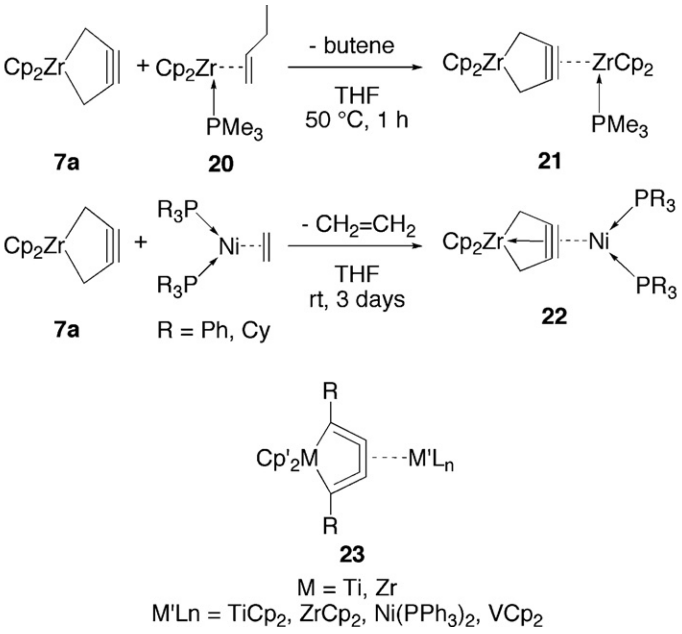


Fig. 12. Molecular structure of **19** (Ar = p-tolyl, R = SiMe$_3$); selected bond lengths (Å) and angles (°).



Scheme 9. Coordination of 1-metallacyclopent-3-yne to other metals.

In the absence of phosphine ligands, **7a** gave a symmetric bimetallic complex **24Zr** [119]. The titanium complex **24Ti** was reported by Rosenthal prior to our report [106].

Probably the intermediate **21**′ formed and the α-carbon atom migrated to the other metal, although it is unclear yet (Scheme 10). Indeed, we achieved the interconversion between **21** and **24Zr** by adding and removing the phosphine ligand. The bond length of the C–C triple bond increased in the order **7a** < **21** < **24Zr** (Table 6).

5.3. Reactions with electrophiles

5.3.1. Reactions with acids

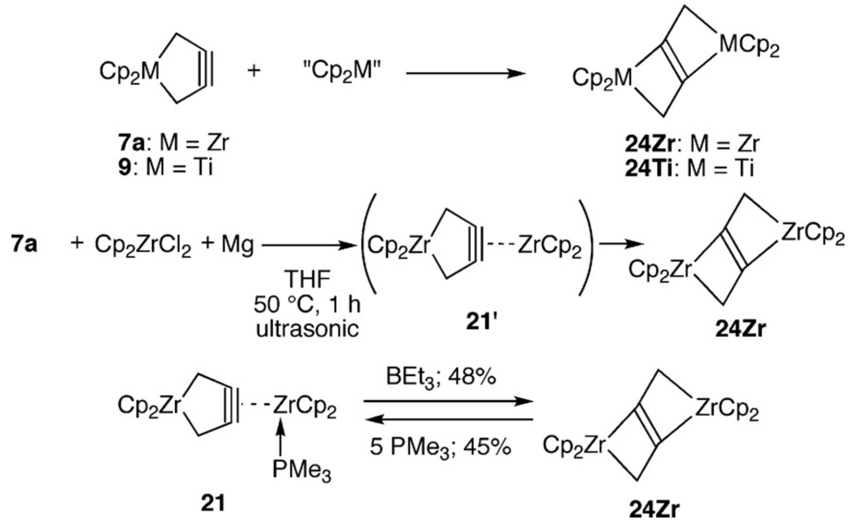
Protonolysis of **2** by aqueous HCl gave exclusively 1,4-disubstituted 2-butynes, while non-substituted complex **7a** gave a mixture of 2-butyne and 1,2-butadiene in 29% and 55% yield, respectively (Scheme 11) [151].

Deuterolysis resulted in incorporation of deuterium at the 1- and 4-positions of 2-butyne and the 3- and 4-positions of 1,2-butadiene. Interestingly, a reaction with anhydrous hydrogen chloride in diethyl ether (1.0 M) gave 1,2-butadiene selectively.

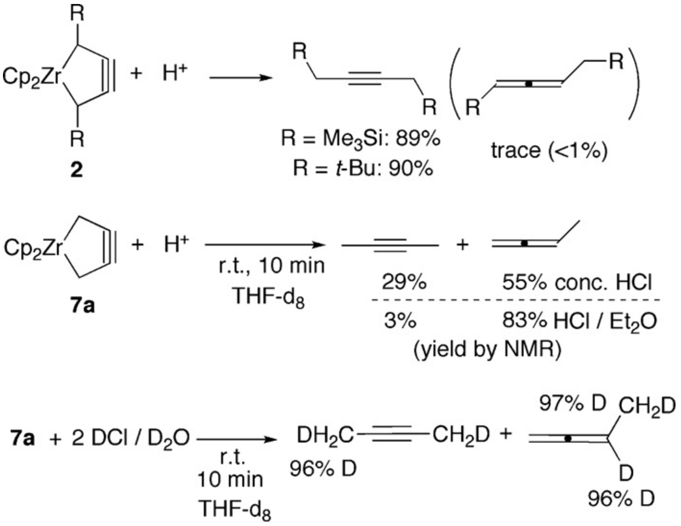
Table 6
Bond lengths (Å) and angles (°) of 1-zirconacyclopent-3-yne **7a** and the bimetallic complexes **21** and **24Zr**.

	7a	21	24Zr
Zr–C1	2.415(3)	2.279(4)	2.230(7)
(Zr–C4)	2.428(3)	2.270(3)	
Zr–C2	2.314(3)	2.495(3)	2.399(6)
(Zr–C3)	2.320(3)	2.461(3)	2.196(6)[a]
C1–C2	1.406(4)	1.490(4)	1.504(8)
(C3–C4)	1.408(5)	1.480(4)	
C2–C3	1.237(5)	1.336(4)	1.38(1)[b]
C1–C2–C3	151.5(3)	136.7(3)	129.6(7)[c]
(C2–C3–C4)	151.3(3)	140.6(3)	

[a] Zr–C2*.
[b] C2–C2*.
[c] C1–C2–C2*.

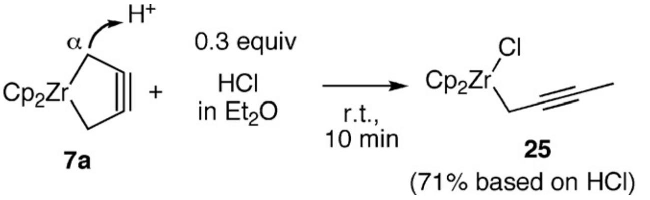


Scheme 10. Formation of bimetallic complexes.



Scheme 11. Protonolysis of 1-zirconacyclopent-3-ynes.

We examined the reaction of **7a** with 0.3 equiv of HCl in Et_2O to investigate the first step of the reaction. Protonated species (2-butynyl)chlorozirconocene **25** was observed by NMR spectroscopy (Eq. (7)). When complex **7a** was treated with an equimolar amount of HCl/Et_2O, we observed 2-butyne, 1,2-butadiene, Cp_2ZrCl_2 and unreacted **7a**, and no intermediates were detected.

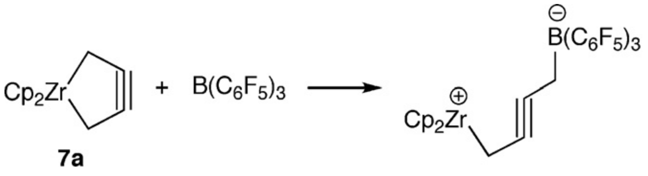


(7)

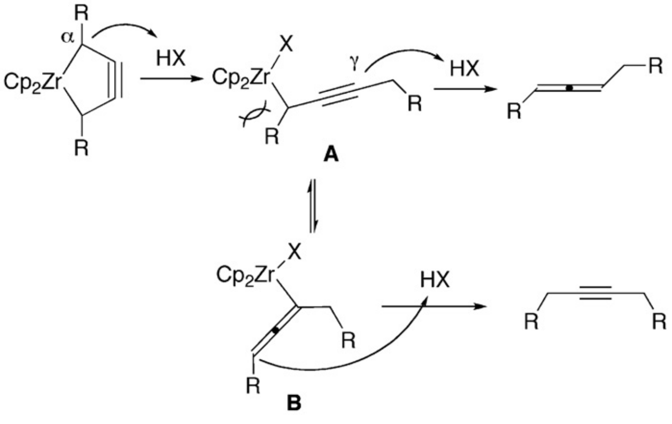
These results suggest that the second protonation proceeded much faster than the first protonation. This is in a sharp contrast to the cases of other zirconacyclic compounds in which the second protonolysis is much slower than the first protonation [152,153]. This difference is probably because of the high reactivity of propargyl intermediate **25** toward electrophiles. The different selectivity in **2** and **7a** can be rationalized by steric effects in the intermediate. It has been commonly observed in a variety of propargyl metal compounds that these species are in equilibrium with allenyl species, and that their nucleophilic attack occurs at the γ-position [154–162].

The first protonation of **7a** form 2-butynyl species **25**. The second protonation probably occurs at the γ-position to give 1,2-butadiene selectively. The substituted complex **2** affords the 2-butynyl species **A** first, where **A** is in equilibrium with **B**. The equilibrium favors **B** for steric reasons when R is large substituents. The second protonation proceeds at the γ-position of **B**. Although the effect of aqueous conditions is still unclear, it may affect the equilibrium between **A** and **B** (Scheme 12).

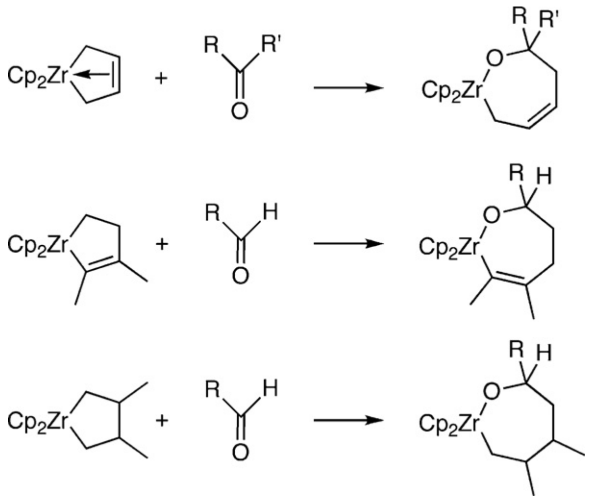
Rosenthal reported that tris(pentafluorophenyl)borane, a Lewis acid, reacted with **7a** at the α-position to cleave of the Zr–C bond (Eq. (8)) [163,164].



(8)



Scheme 12. Propargyl and allenyl species in protonolysis.



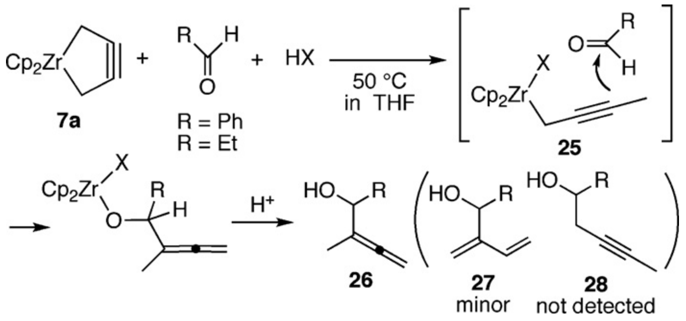
Scheme 13. Reactions of zirconacycles with aldehydes and ketones.

5.3.2. Reactions with aldehydes, ketones, and isocyanides

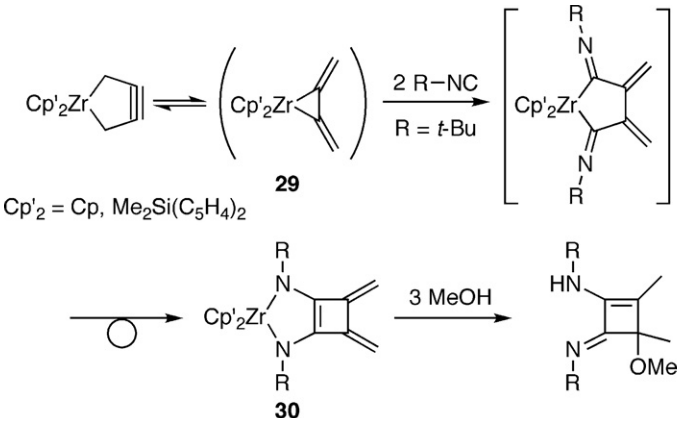
It has been reported that zirconacycle compounds such as 1-zirconacyclopent-3-ene (*s-cis*-1,3-butadiene complex) [165], 1-zirconacyclopent-2-ene and 1-zirconacyclopentane [166] readily react with ketones or aldehydes to give seven-membered oxazirconacycles (Scheme 13).

The 1-zirconacyclopent-3-yne **7a**, however, did not react with aldehydes or ketones under normal conditions, while a preliminary study showed that **2a** reacted with ketones to give a double insertion product [167]. Thus nucleophilic attack of the protonated species **25** on aldehydes was studied. It has been reported that propargylzirconium species react with carbonyl compounds to give β-allenyl alcohols [162]. We added a proton source such as ammonium salt to the mixture of **7a** and benzaldehyde (Scheme 14) [151]. Hydrolysis of the reaction mixture gave an allenylated alcohol, 2-methyl-1-phenyl-2,3-butadien-1-ol (**26**) in moderate yields. The isomer, 2-methylene-1-phenyl-3-buten-1-ol (**27**), was formed as a minor product, and the selectivity was excellent in most cases. The 2-butynylated alcohol **28** was not detected. On the other hand, the reaction using triethylammonium tetraphenylborate in 1,2-dichloroethane resulted in the selective formation of **27**. Presumably, the first protonolysis by [NEt$_3$H][BPh$_4$] occurred at the γ-position for steric reasons to give a cationic 2,3-butadienylzirconium species that reacted with the aldehydes.

Rosenthal reported insertion of isocyanide to Zr–C in 1-zirconacyclopent-3-ynes that gave the diazazirconacycle product **30** [168]. In this reaction they suggested the transformation of 1-zirconacyclopent-3-yne into η^2-π-coordinated butatriene complex **29** (Scheme 15). It is likely that isocyanides insert into this species to form the cyclobutene structure, although the intermediates have not been observed. We obtained information on the mechanism on the isocyanide insertion (vide infra).



Scheme 14. Reaction of **7a** and aldehyde in the presence of HX.

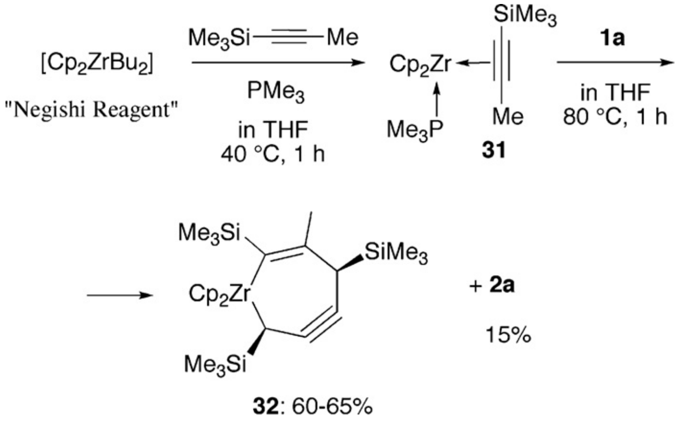


Scheme 15. Insertion of isocyanide into the Zr–C bond in 1-zirconacyclopent-3-ynes.

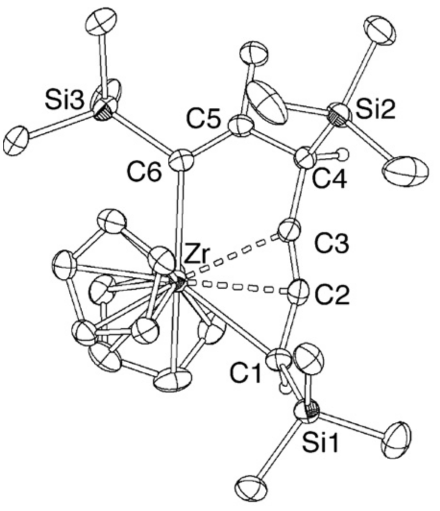
5.4. Formation of seven-membered cycloalkynes

As far as we attempted, 1-zirconacyclopent-3-yne complexes such as **2** and **7** did not react with alkynes under usual conditions. Alkynes, however, can couple with **1a** on the zirconium to afford seven-membered metallacycloalkynes if the reaction is started with zirconocene–alkyne complexes [169]. In the preparation of **2a**, the zirconocene-but-1-ene complex generated in situ from Negishi reagent was used. The butatriene **1a** replaces but-1-ene on zirconium to afford **2a**, and the coupling products of but-1-ene and butatriene were not observed. On the other hand, when the zirconocene–alkyne complex, Cp$_2$Zr(Me$_3$Si–C≡C–Me)(PMe$_3$) (**31**) [17,125,170,171], was treated with **1a**, the coupling of alkyne and **1a** took place to give **32** in 60–65% yield accompanied by the formation of a small amount of **2a** (15% by ^{1}H NMR) (Scheme 16).

X-ray diffraction analysis showed that **32** has a distorted seven-membered metallacyclic structure (Fig. 13). The stereochemistry of the two trimethylsilyl groups was the *syn*-form in contrast with five-membered cycloalkynes. The formation of the *anti*-form was negligible judging from the NMR spectra of the reaction mixture. The length of Zr–C1 (2.580(2) Å) demonstrates the existence of the metal-carbon bond. The C2–C3 bond is short enough (1.239(3) Å) to be regarded as a triple bond. The alkyne moiety is bent toward the metal, showing its interaction with the Zr atom. The angles C1–C2–C3 and C2–C3–C4 are 156.1(2)° and 159.3(2)°, respectively.

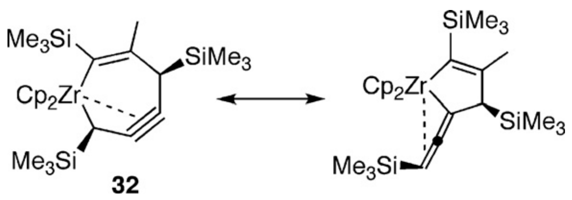


Scheme 16. Preparation of 1-zirconacyclohept-2-en-5-yne **32**.



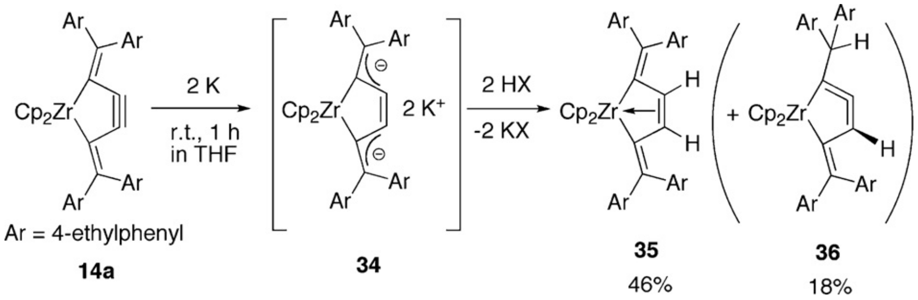
Zr-C1	2.580(2)
Zr-C2	2.417(2)
Zr-C3	2.425(2)
Zr-C6	2.424(2)
C1-C2	1.383(3)
C2-C3	1.239(3)
C3-C4	1.465(3)
C4-C5	1.512(3)
C5-C6	1.358(3)
Zr-C1-C2	67.5(1)
Zr-C3-C4	125.1(1)
C3-Zr-C6	65.8(1)
C1-C2-C3	156.1(2)
C2-C3-C4	159.3(2)
C3-C4-C5	106.6(2)
C4-C5-C6	120.2(2)
C6-C5-C7	127.7(2)

Fig. 13. The molecular structure of **32**. Drawn with 50% probability. Hydrogen atoms are partly omitted for clarity.



Scheme 17. Seven-membered alkyne or α-vinylidene-1-zirconacyclopent-2-ene.

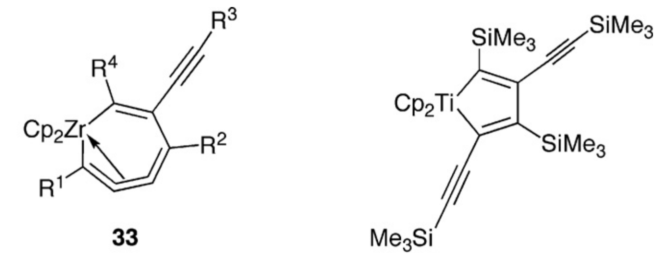
The short Zr–C2 and Zr–C3 distances also support metal-carbon interactions. The C1–C2 (1.383(2) Å) is significantly longer than C2–C3, and that the angle C2–C3–C4 is much larger than 120°. These results suggest the 1-metallacyclohept-2-en-5-yne structure of **32**, although the C1–C2 bond is too short to be regarded as a single bond.



(9)

The methine proton at C1 appeared at 2.17 ppm in the ^{1}H NMR spectrum, showing its sp^3 character. The C2 and C3 signals appeared at 101.36 and 110.05 ppm in the ^{13}C NMR spectrum, which could be regarded as alkyne carbons. The signal for C1 was observed at 38.8 ppm. In the infrared spectroscopy, absorption due to the triple bond was observed at 2028 cm^{-1}. A resonance structure with an α-allenylidene-1-zirconacyclopent-2-ene can also be considered (Scheme 17).

These results may remind one of seven-membered zirconacyclocumulene complexes **33** reported independently by Rosenthal and Buchwald [34,172]. These cyclocumulene complexes, which were prepared from coupling of two equiv of 1,3-diynes showed a seven-membered structure when the central metal was zirconium, while the titanium analogue showed an α-alkynyl-1-metallacyclopenta-2,4-diene structure (Fig. 14) [173].



$R^{1\text{-}4}$ = Me_3Si, *t*-Bu, Ph etc.

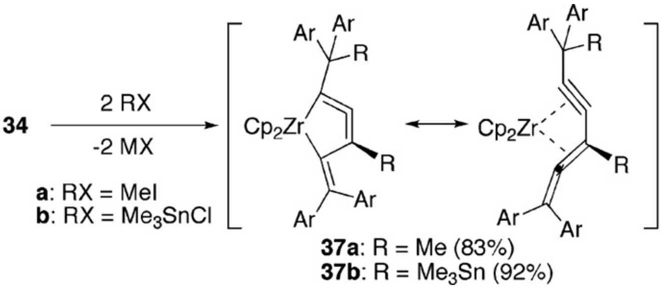
Fig. 14. Seven-membered cumulene complex and α-alkynyl complex.

6. Reactions of [5]cumulene complexes

6.1. Transformation into 1-metallacyclopenta-2,3-dienes

We found that the 1-zirconacyclopent-3-yne complexes were unexpectedly inert to various reactants. We reasoned that 1-metallacyclopent-3-ynes of conjugated systems would be more reactive. We recently reported the synthesis of a 2,5-bisalkylidene-1-metallacyclopent-3-yne compound and its transformation into 1-metallacyclopent-3-ene and formal "1-metallacyclopenta-2,3-diene" compounds. It was reported that tetraarylbutatrienes and hexapentaenes readily form dianion species by treatment with alkali metals [174–176]. We found that the complex of tetrakis(4-ethylphenyl)hexapentaene **14a** underwent two-electron reduction [68]. For example, **14a** was treated with potassium graphite to give dianionic species **34**, and protonation of **34** resulted in 1-zirconacyclopent-3-ene **35**. The metallacycle of **35** was bent at the α-carbons by 35°, showing that the complex has the metallacyclopent-3-ene structure, while the angle was smaller than those of the reported *s-cis* 1,3-diene complexes (60–67°) [177,178]. The ^{1}H NMR spectra of the reaction mixture suggested formation of **36**, although it has not been isolated so far (Fig. 15).

Treatment of **34** with two equiv of iodomethane afforded dimethylated product **37a**, which has a formal cumulative double bond in the five-membered metallacyclic structure. Trimethyltin chloride reacted similarly with **34** to give **37b**.



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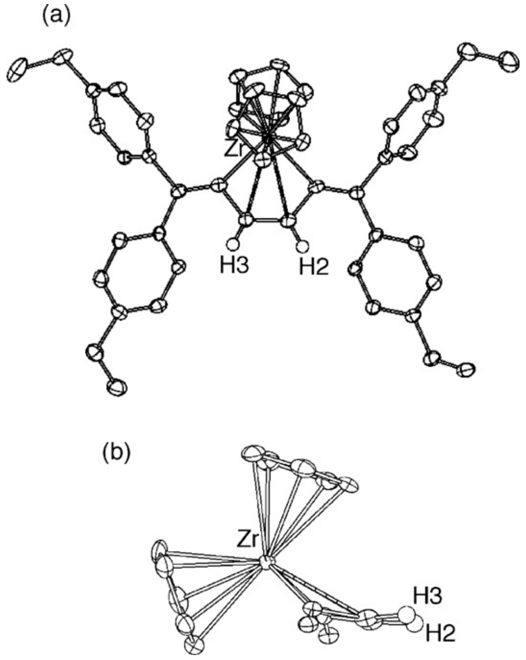
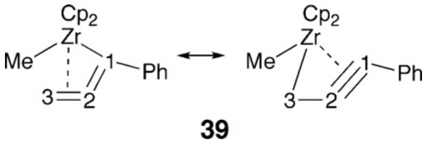


Fig. 15. ORTEP drawing of **35**; (a) top view, (b) side view. Aryl groups are omitted in (b) for clarity.

These complexes are stable and isolable five-membered cycloallene compounds, and **37a** was unambiguously characterized. Erker and coworkers reported hafnium and zirconium complexes **38** of similar structures [69,70]. They prepared these complexes from bis(alkynyl)metallocene compounds via 1,1-hydroboration (Scheme 18).

According to the protocol adopted for 1-metallacyclopen-3-enes, 1-metallacyclopent-3-ynes and 1-metallacyclo-2,3,4-trienes, 1,3-enynes must give 1-metallacyclopenta-2,3-dienes, i.e., cycloallene complexes. However, there have been scarcely any η^4-coordinated 1,3-dienes reported. Polymeric platinum complexes have been suggested on the basis of infrared spectra [179]. The ruthenium complex of η^6-1,3,5-dienyne was unequivocally characterized, although the complex readily underwent aromatization at rt to form a Ru-arene complex [180].

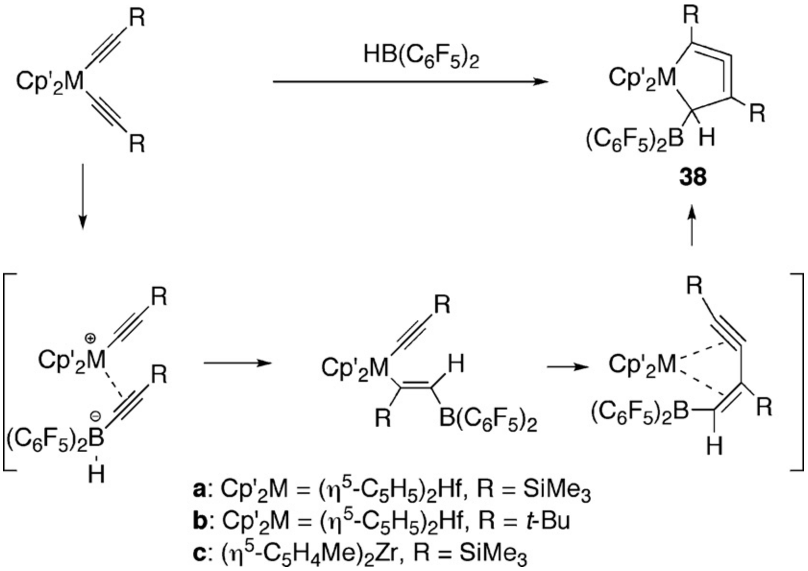


Scheme 19. Allenyl-propargyl species.

As discussed in the previous section on the 1-metallacyclopent-3-ynes, the same question of whether these products **37**, **38** should be regarded as η^4-1,3-enyne complexes or 1-metallacyclopenta-2,3-dienes can be raised (Eq. (10)). Five-membered cycloallenes have been reported only as short-lived species [80,81], while complex **37a** is very stable at rt if kept under argon as crystals. The structure of **37a** is shown in Fig. 16. The five-membered metallacycle plane is folded at the Zr–C3 bond, such that it looks like a half-and-half mixture of a 1-metallacyclopenta-2,3,4-triene and a 1-metallacyclopent-3-ene. The C1–C2 distance and the C1–C2–C3 angle are in the same range as those of the former (1.28–1.30 Å, and 147–152°) [34,181]. The C3–C4 distances and C2–C3–C4 angles, on the other hand, resemble those in the latter (1.45–1.47 Å and 122.7–123.5°) [177]. The sum of the three bond angles at C3 (358.4°) indicates its sp^2 character. Judging from these facts, the C2–C3 bond could be a double bond that is longer as a result of coordination to the metal, as observed in 1-zirconacyclopent-3-enes (Table 7).

Wojcicki and coworkers reported an η^3-phenylallenyl zirconocene complex **39** (Scheme 19), proposing a combination of η^3-propargyl and η^3-allenyl resonance structures [182]. The lengths C2–C3 and C3–C4 in **39** were 1.259 and 1.354 Å, with an angle of 155.4° (C2–C3–C4). The structural similarity between **37** and **39** implies that **37** should also have such resonance structures. In-plane interaction between the internal double bond and the metal center across the five-membered ring also should be considered [70].

Chemical shifts in ^{13}C NMR spectroscopy are summarized in Table 8. Central carbon atoms of allenes generally appear downfield, such as 200 ppm [183]. We note that C2 appeared at 128.8



a: $Cp'_2M = (\eta^5\text{-}C_5H_5)_2Hf$, R = $SiMe_3$
b: $Cp'_2M = (\eta^5\text{-}C_5H_5)_2Hf$, R = *t*-Bu
c: $(\eta^5\text{-}C_5H_4Me)_2Zr$, R = $SiMe_3$

Scheme 18. Formation of cycloallene complexes **38** from bis(alkynyl)metallocenes.

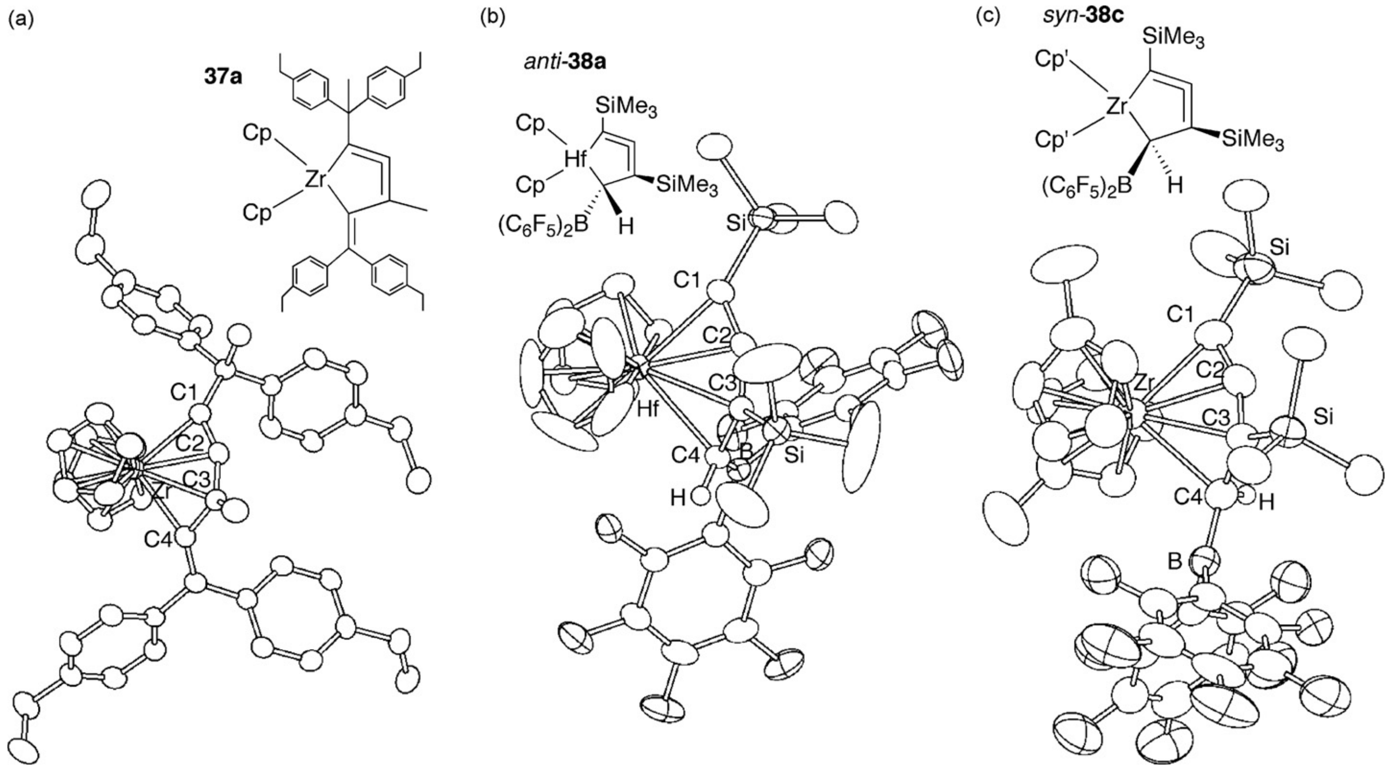


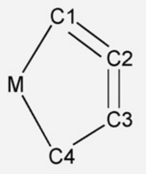
Fig. 16. Molecular structure of metallacycloallenes.

(**37a**) and 123.3 ppm (**37b**). These values seem inconsistent with an "allene structure". Again, the chemical shifts of **37** were similar to those of **39**, where the quaternary carbon (C2) was observed at 114.1 ppm. Six-membered trisilacycloallenes showed their allene sp-carbon at 207 ppm although the allene was bent by 161 and 166° [184,185]. Diphosphacycloallene was also at 207 ppm with a bent angle of 156° [186]. These suggest that the upfield shift of the allene center carbon of **37** in ^{13}C NMR is not a result of the bent structure.

The ^{13}C–^{13}C coupling constants between C1 and C2 were 79 Hz (**37a**) and 83 Hz (**37b**), and between C2 and C3 were 73 Hz (**37a**) and 65 Hz (**37b**). These are smaller than the typical values for allenes (99–103 Hz) [187,188] or acetylene (170 Hz), but a little larger than that of ethylene (68 Hz) [189]. Although $^1J_{CC}$ values in bent allenes have not been studied well, these may support the resonance structure in Eq. (10).

Recently Bertrand et al. reported bent allene compounds **40** which is bent by 135°, the center carbon appearing at 112 ppm

Table 7
Selected bond lengths and angles in 1-metallacyclopenta-2,3-dienes.

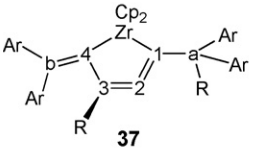


	37a	*anti*-38a	*syn*-38c
M–C1	2.323(3)	2.340(3)	2.380(4)
M–C4	2.299(2)	2.494(3)	2.520(4)
C1–C2	1.286(4)	1.276(4)	1.276(6)
C2–C3	1.372(4)	1.356(4)	1.379(6)
C3–C4	1.439(4)	1.490(4)	1.478(6)
C1–C2–C3	153.6(3)	156.4(3)	158.4(5)
C2–C3–C4	120.5(2)	119.2(3)	112.4(4)
Σ at C3[a]	358.5	359.8	358.7
Angle at M–C3[b]	35.3	42.0	51.8
Refs.	[68]	[69]	[70]

[a] The sum of the three bond angles except for the M–C3 bond.

[b] The angle between the two planes at M–C3 bond. One plane includes M–C1–C2–C3, and the other does M–C3–C4.

Table 8
Chemical shifts (ppm) in ^{13}C NMR spectroscopy.



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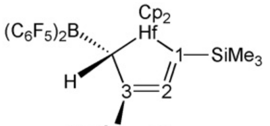
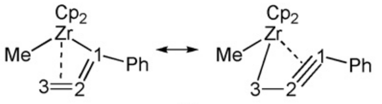


38a



39

	37a (R = Me)[a]	**37b** (R = SnMe$_3$)[a]	**38a**[b]	**39**[c]
Ca	51.7	54.0		
C1	149.3	126.8	114.4	120.5
C2	128.8	123.3	136.2	114.1
C3	81.6	67.3	93.7	55.5
C4	185.6	187.7		
Cb	146.6	141.3		
Refs.	[68]	[68]	[69]	[182]

[a] In C_6D_6.

[b] In $C_6D_5CD_3$, at 233 K.

[c] In CD_2Cl_2.

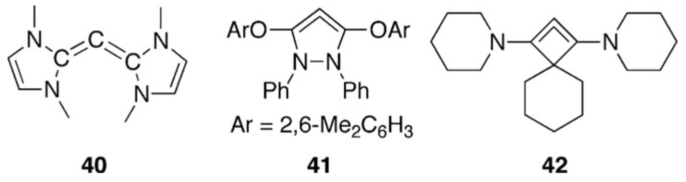


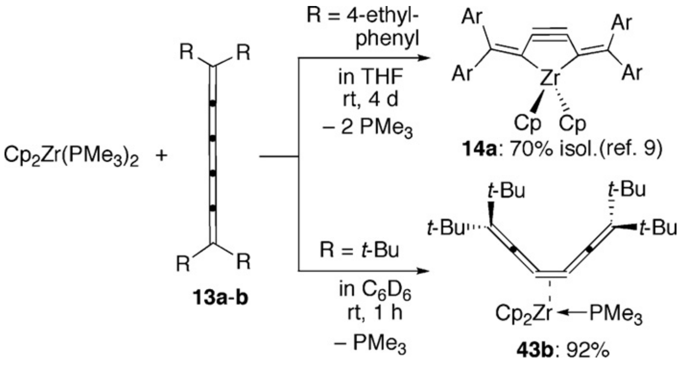
Fig. 17. Stable bent allenes.

[190]. They even reported “five-membered cycloallene” **41** [83] and an all-carbon cyclobuta-1,2-diene **42** [84] although these are still controversial [191,192]. Schrock reported four-membered “deprotio”metallacyclobutadienes [193,194]. The metallalcycloallene compounds also must be considered related to these compounds (Fig. 17).

6.2. “Haptotropic” shift in hexapentaene complexes

Many examples of η^2-π-complexes of [*n*]cumulenes have been reported, while we reported the 1-metallacyclopent-3-yne complexes. Haptotropic interconversion between these two has scarcely been reported. As shown in Scheme 15, Rosenthal and co-workers suggested the possibility of η^2-butatriene complexes **29** as intermediates in the insertion reactions of isocyanide into 1-zirconacyclopent-3-ynes such as **7a** [168], although these species **29** were not detected. We reported zirconocene–hexapentaene complexes that show haptotropic behavior. The reaction of $Cp_2Zr(PMe_3)_2$ and 1,1,6,6-tetrakis(*tert*-butyl)-1,2,3,4,5-hexapentaene (**13b**) [91], afforded the phosphine-coordinated η^2-π-complex **43b** in excellent yield, whereas aryl-substituted [5]cumulene gave the 1-zirconacyclopent-3-yne **14a** (Scheme 20). Cycloalkyne complex **14b** could be prepared from **13b** and Cp_2ZrCl_2/Mg in the absence of PMe_3.

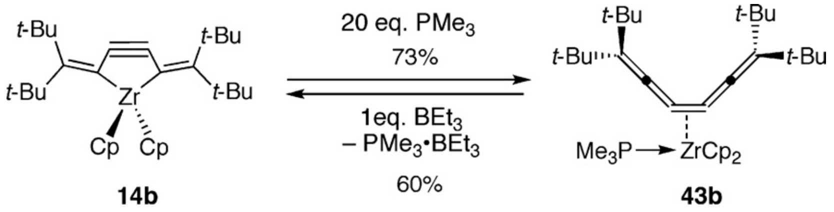
It is interesting that **14b** was converted into **43b** in the presence of trimethylphosphine, and **43b** into **14b** by addition of triethylborane (Scheme 21). This is the first example of a haptotropic interconversion between an η^2-cumulene complex and a 1-metallacyclopent-3-yne [195]. The molecular structures of both **14b** and **43b** were unequivocally determined (Fig. 18).



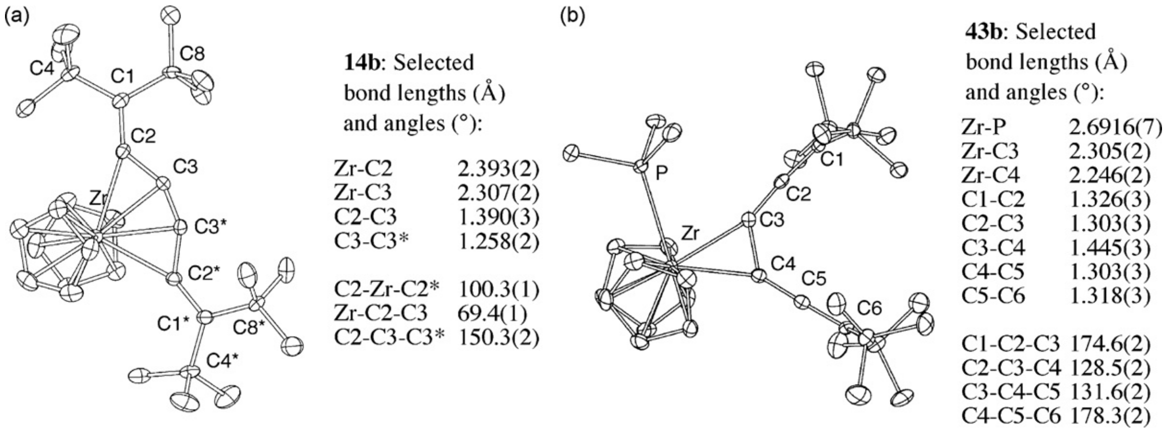
Scheme 20. Formation of η^2-π-complex and 1-zirconacyclopent-3-yne.

The bond lengths and angles around the Zr, C3, and C4 atoms in **43b** resemble those in zirconium-alkene complexes [123,124]. It is noteworthy that the distances Zr–C3 in **14b** and Zr–C3, Zr–C4 in **43b** are in the same range. Insertion of *tert*-butylisocyanide took place both on **14b** and **43b** at rt to give the double-inserted product **45** in good yields [196–198]. Interestingly, the η^2-complex isocyanide-adduct **44** was formed during the reaction of **43b** with *t*-BuNC. The molecular structure of **44** was unambiguously characterized (Fig. 19).

The reaction of **14b** and two equiv of *t*-BuNC was observed by ^{1}H NMR spectroscopy. Formation of **44** (24%) and **45** (29%) was observed after 3 h. Complex **45** increased as the amount of **44** decreased, reaching 82% in 18 h. These results clearly indicate that a ligand-induced haptotropic shift from **14b** to **44** was the first step in the insertion of isocyanides (Scheme 22).



Scheme 21. Reversible haptotropic conversion between **14b** and **43b**.



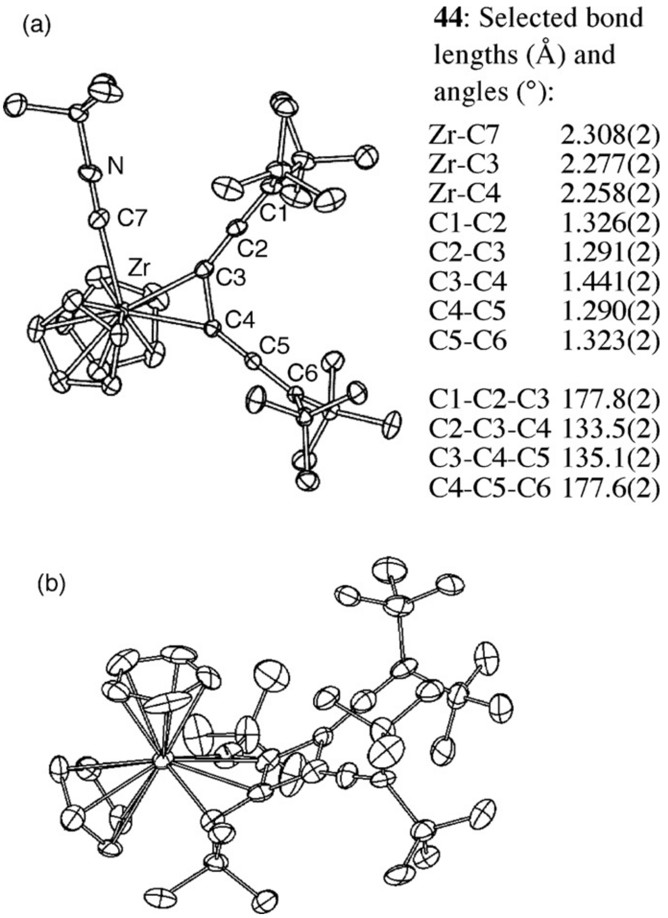
14b: Selected bond lengths (Å) and angles (°):

Zr-C2	2.393(2)
Zr-C3	2.307(2)
C2-C3	1.390(3)
C3-C3*	1.258(2)
C2-Zr-C2*	100.3(1)
Zr-C2-C3	69.4(1)
C2-C3-C3*	150.3(2)

43b: Selected bond lengths (Å) and angles (°):

Zr-P	2.6916(7)
Zr-C3	2.305(2)
Zr-C4	2.246(2)
C1-C2	1.326(3)
C2-C3	1.303(3)
C3-C4	1.445(3)
C4-C5	1.303(3)
C5-C6	1.318(3)
C1-C2-C3	174.6(2)
C2-C3-C4	128.5(2)
C3-C4-C5	131.6(2)
C4-C5-C6	178.3(2)

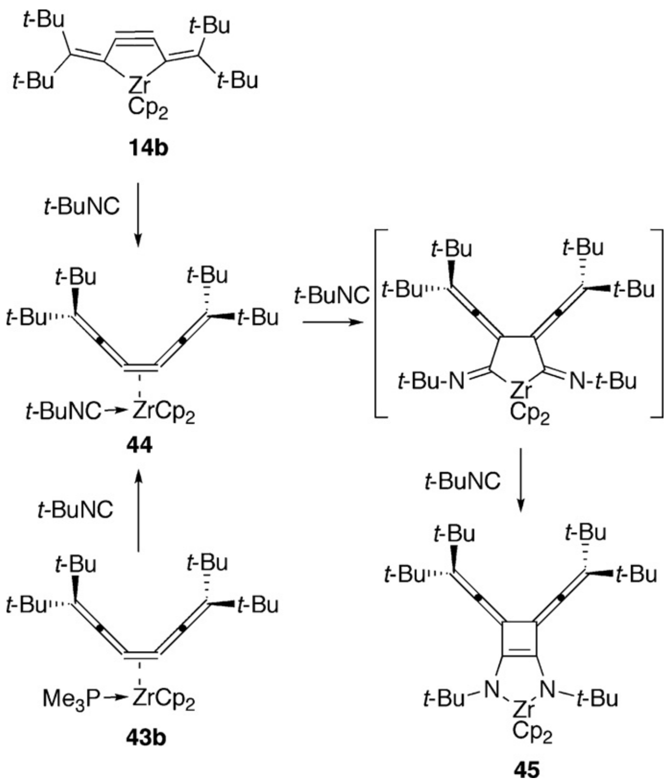
Fig. 18. Molecular structures of **14b** (top) and **43b** (bottom). Drawn with 50% probability. Hydrogen atoms are omitted.



44: Selected bond lengths (Å) and angles (°):

Zr-C7	2.308(2)
Zr-C3	2.277(2)
Zr-C4	2.258(2)
C1-C2	1.326(2)
C2-C3	1.291(2)
C3-C4	1.441(2)
C4-C5	1.290(2)
C5-C6	1.323(2)
C1-C2-C3	177.8(2)
C2-C3-C4	133.5(2)
C3-C4-C5	135.1(2)
C4-C5-C6	177.6(2)

Fig. 19. Molecular structure of **44** (a) and **45** (b).



Scheme 22. Insertion of *tert*-butylisocyanide.

7. Summary

We have shown that coordination of [*n*]cumulenes to transition metals bring about not only η^2-π-coordinated complexes but also 1-metallalcyclopent-3-yne compounds. Some reactivities of these novel compounds were shown, such as protonolysis and coordination. Hexapentaenes, [5]cumulenes, showed more varied reactivity and transformed into 1-metallacyclopenta-2,3-diene or converted into an η^2-π-complex. However, studies on this series of novel complexes have just started, and there still remain many questions. All 1-metallacyclopent-3-ynes and 1-metallacyclo-2,3-dienes have been prepared using group 4 metals, and there have been no examples of other group metals. Is it possible to synthesize them with other metals? There have been no examples with [4]-, [6]- or [7]cumulenes. Is interconversion between polyyne complexes and cumulene complexes possible? The reactivity of the complexes has not been well investigated. Reactivity toward electrophiles and/or nucleophiles and redox chemistry are to be studied, including potential applications.

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