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Synthesis and structure of 1-metallacyclopent-3-yne complexes of group 4 metals ☆

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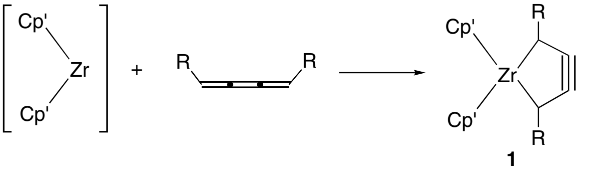
Abstract

Five-membered metallacyclic alkyne complexes of titanium and hafnium, 1,1-bis(cyclopentadienyl)-1-titanacyclopent-3-yne (**2**) and *trans*-1,1-bis(cyclopentadienyl)-2,5-trimethylsilyl-1-hafnacyclopent-3-yne (**6**), were synthesized and structurally characterized. The structural analysis of titanium complex **2** implied a larger contribution of an η^4-π,π-coordinated structure. The hafnium compound **6** has a similar structure to the corresponding zirconium analogue (**1a**), although slight differences in the bond lengths and angles were observed. A novel 1-zirconacyclopent-3-yne complex, 1,1-bis(methylcyclopentadienyl)-2,5-bis(trimethylsilyl)-1-zirconacyclopent-3-yne (**5**), was also prepared and the structure of the *trans*-isomer was determined.

Keywords: Titanium; Hafnium; Zirconium; Metallacyclopentyne; Butatriene

1. Introduction

It is known that small cyclic alkynes are generally very unstable and difficult to isolate [1–3]. In particular, cyclopentynes, five-membered cyclic alkynes, are highly reactive and short-lived species. Hydrocarbyl cyclopentyne and thiacyclopentyne [4] have been prepared, and the formation was spectroscopically detected [5–7] or confirmed by trapping them by subsequent chemical reactions, such as 2 + 2 cycloaddition [8], metal complexation [9–11], and so on. However these compounds are so reactive that they have not been isolated in a pure form.



1

a: Cp' = C_5H_5, R = $SiMe_3$
b: Cp' = C_5H_5, R = *t*-Bu
c: Cp' = C_5H_5, R = H
d: Cp' = C_5H_4-*t*-Bu, R = H

(1)

We recently reported the synthesis and structure of metallacyclic compounds derived from zirconocene and 1,2,3-butatriene and noted that the complexes could be regarded as the first isolable five-membered cyclic alkynes, i.e., 1-zirconacyclopent-3-ynes (Eq. (1)) [12]. We also reported a simple and versatile preparative method for "non-substituted" 1-zirconacyclopent-3-ynes (**1c**–**d**: R = H) and showed their reactivity [13–16].

☆ This paper is dedicated to Prof. Ei-ichi Negishi (Herbert C. Brown Distinguished Professor at Purdue University) on the occasion of his 70th birthday.

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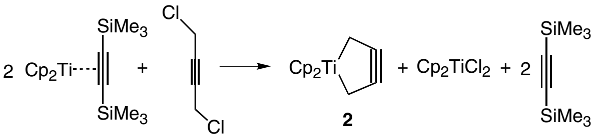
Five-membered metallacyclocumulenes reported by Rosenthal and coworkers showed similar structure and reactivity to metallacyclopentynes [17–20]. They have prepared a variety of zirconacyclocumulenes as well as titanacyclocumulenes and extensively studied their reactivity, although a hafnium analogue has not been reported. They demonstrated that these zirconium and titanium complexes showed a few slight differences in their molecular structures [21].

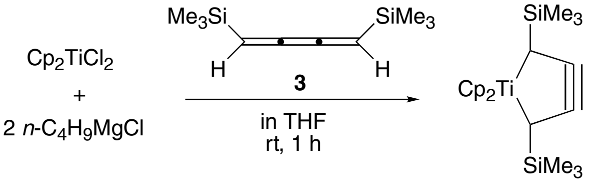


(2)

It is important to compare the structure of zircona-, titana- and hafnacyclopentyne complexes to understand their properties. Thus, we aimed to synthesize metallacyclopentynes of other group 4 metals [22]. Recently, Rosenthal and coworkers have reported preparation of a 1-titanacyclopent-3-yne compound **2**, although the molecular structure of **2** was not determined (Eq. (2)) [23]. Herein, we wish to report the first examples of structurally characterized 1-metallacyclopent-3-yne complexes of titanium and hafnium. A part of this work has previously been communicated [24].

2. Results and discussion

2.1. Synthesis of 1-titanacyclopent-3-ynes



4

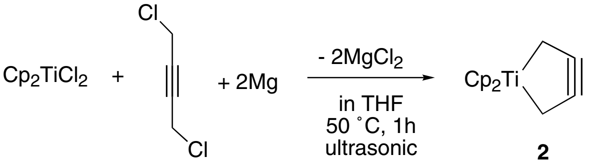
76% (^{1}H NMR)

cis/trans = 33/67

(3)

We first prepared 1,1-bis(cyclopentadienyl)-2,5-bis(trimethylsilyl)-1-titanacyclopent-3-yne (**4**) from Cp_2TiCl_2 and (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**3**) [25,26] (Eq. (3)). Titanocene dichloride was treated with 2 equiv. of *n*-BuMgCl, and then reacted with **3**. The volatiles were removed in vacuo and the residue was dissolved in C_6D_6. NMR observation of the solution indicated the formation of 1-tianacyclopent-3-yne **4** as a mixture of *cis*- and *trans*-isomers in good yield. Two signals of the cyclopentadienyl (Cp) rings were observed at 4.86 and 5.03 ppm for the *cis*-isomer and one singlet at 4.94 ppm for the *trans*-isomer. These signals appeared slightly upfield compared with the zirconium analogue **1a** (5.00 and 5.36 ppm for *cis*, 5.18 ppm for *trans*). The signals for the methine protons, on the other hand, appeared at 2.49 and 2.28 ppm for the *cis*- and *trans*-isomers, respectively, being observed downfield relative to **1a**. ^{13}C NMR spectroscopy revealed that signals assignable to quaternary alkynyl carbons in the *cis*- and *trans*-isomers were observed at 107.96 and 108.80 ppm, respectively. These spectra were similar to those of the zirconium complex **1a**, supporting the formation of **4**. The isomerization from the *cis*-isomer to the *trans*-isomer reached equilibrium after 1 h at r.t. This is faster than observed for the zirconium analogue **1a**, where it required overnight stirring at r.t. Although it is still unclear how the complexes isomerize from *cis* to *trans*, one possible explanation is that it takes place via β-hydrogen elimination from η^2-π-coordinated form [12]. Our preliminary observation were that (*Z*)-**3** isomerized to (*E*)-**3** in the presence of *catalytic* amount of zirconocene species [12]. Another possibility is that it involves a dimeric intermediate as Negishi proposed for zirconium-catalyzed *cis*/*trans* isomerization of 1,2-diarylethenes [27].

Our attempt to isolate **4** by recrystallization, however, has been unsuccessful so far. Judging from NMR spectroscopy, **4** decomposed to unidentified species during the operation. Next we prepared the 1-titanacyclopent-3-yne compound derived from 1,4-dichlorobut-2-yne. The procedure was similar to the preparation of the zirconium derivative **1c** (Eq. (4)).



(4)

1-Titanacyclopent-3-yne **2** was formed in 60% yield by ^{1}H NMR. Recrystallization from hexane solution gave dark brown crystals of **2**, albeit in low yield (9%). Spectroscopic data were identical to the reported results [23]. The molecular structure of **2** was determined by an X-ray diffraction study (Fig. 1). This is the first example of a structurally characterized 1-titanacyclopent-3-yne. Its structure is similar in principle to that of the corresponding zirconium complex **1c** [13,14]. The four carbons of butatriene and Ti metal are coplanar, and the butatriene moiety is bent

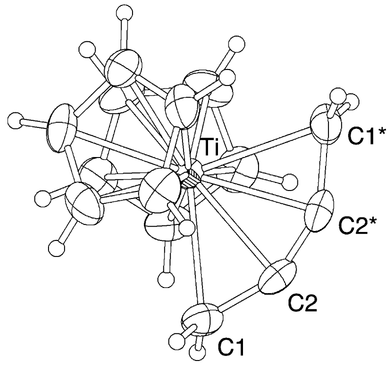


Fig. 1. Molecular structure of **2**. Drawn with 50% probability.

to form a strained five-membered metallacycle. The bond lengths and angles are compared to those of the zirconium complexes in Table 1. The Ti–C1 and Ti–C2 distances are significantly shorter than the Zr–C1/C4 and Zr–C2/C3 distances of **1c**. Shorter Ti–C bonds compared with the corresponding Zr–C bonds are usually observed. For example, in $Cp_2M(CH_3)_2$ complexes, the M–C lengths are 2.17–2.18 (M = Ti) and 2.27–2.28 Å (M = Zr) [28,29]. It is noteworthy that the C1–C2 length is slightly shorter than those in Zr complexes, and C2–C2* is longer. Besides, the summation of the three bond angles (excluding the C–Ti bond) at C1 is 350°, which is larger than those in Zr and Hf complexes(340–345°). These facts imply that the contribution of the η^4-π,π-coordination mode, which was proposed by Lin and coworkers based on calculation [30], in **2** is larger than in **1c** (Fig. 2).

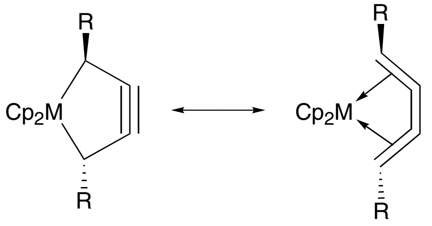
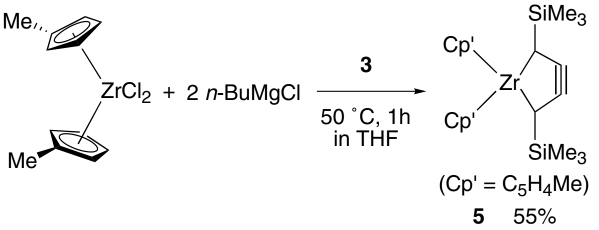


Fig. 2. Resonance structure, η^2-σ,σ and η^4-π,π bonding modes.

2.2. *Synthesis of 1-zirconacyclopent-3-yne complex* **5**



(5)

In our first report on 1-zirconacyclopent-3-yne, we reported the molecular structure of **1a**. To obtain more information about similar compounds, we prepared a novel 1-zirconacyclopent-3-yne compound. Bis(methylcyclopentadienyl)dichlorozirconium and (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**3**) were used as starting materials (Eq. (5)). The complex **5** was formed as a *cis*/*trans* mixture (50/50) in a THF solution. In the ^1H NMR spectra, the *cis*-isomer exhibited two signals for the methyl groups and four signals for the Cp protons. On the other hand, the *trans*-isomer showed only one methyl signal and four Cp protons, indicating the four protons on one Cp ring were unequivalent. This indicated that rotation of the Cp rings is restricted in *trans*-**5**, probably because of the steric repulsion between the methyl group on the Cp rings and the trimethylsilyl group. Recrystallization from ether solution gave colorless crystals of *trans*-**5**. The molecular structure of *trans*-**5** is depicted in Fig. 3. The methyl groups on the Cp rings are located distant from the trimethylsilyl groups, which is consistent with the NMR data. The metallacycle plane was slightly tilted 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. This was also observed in **1a** (86.1(4)°), whereas these two planes are nearly perpendicular in non-substituted metallacyclopentyne compounds such as **1c** and **1d**. Other structural features are fundamentally the same as for **1a**,

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

	2	1c	1d	1a	5	6
C1–C2	1.393(3)	1.406(4)	1.418(3)	1.415(7)	1.412(4)	1.403(7)
C2–C3	1.248(4)[a]	1.237(5)	1.237(3)	1.206(7)	1.231(4)	1.229(7)
C3–C4		1.408(5)	1.417(3)	1.400(6)	1.409(4)	1.407(7)
M–C1	2.353(2)	2.415(3)	2.414(2)	2.500(6)	2.452(3)	2.429(5)
M–C2	2.202(2)	2.314(3)	2.311(2)	2.289(5)	2.295(3)	2.276(5)
M–C3		2.320(3)	2.305(2)	2.289(6)	2.294(3)	2.276(5)
M–C4		2.428(3)	2.433(2)	2.504(4)	2.466(3)	2.431(5)
C1–C2–C3	151.7(1)[b]	151.5(3)	150.8(2)	155.9(7)	153.3(3)	153.0(5)
C2–C3–C4		151.3(3)	152.3(2)	156.2(6)	154.1(3)	153.1(5)
C1–M–C4	103.8(1)[c]	99.9(1)	100.6(1)	98.1(2)	99.7(1)	100.4(2)
M–C1–C2	66.4(1)	68.8(2)	67.7(1)	64.8(3)	66.7(2)	66.8(3)
M–C4–C3		68.6(2)	68.6(1)	64.8(3)	66.2(2)	66.7(3)
Metallacyclopentyne to Cp(c)–M–Cp*(c)[d]	89.3(1)	89.6(4)	89.4(1)	86.1(4)	85.4(1).	86.0(2)
Σ(C1)[e]	349.6	340.8	344.9	344.2	340.1	339.4
Σ(C4)[e]		340.1	346.5	342	345.4	339.6
Refs.	This work	14	13	12	This work	This work

[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.

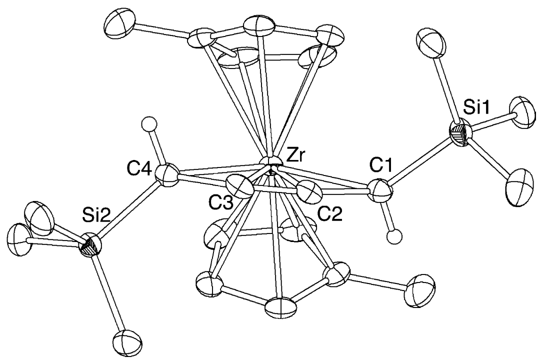
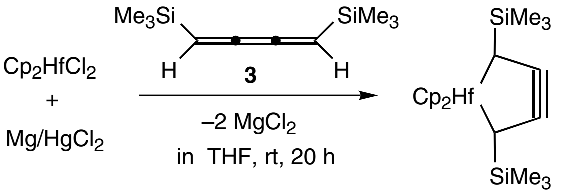


Fig. 3. The molecular structure of **5**. Drawn with 50% probability. Hydrogen atoms are partly omitted for clarity.

although the C2–C3 length (1.231(4) Å) is slightly longer than that of **1a** (1.206(7) Å).

2.3. Synthesis of 1-hafnacyclopent-3-yne complexes



6
73% (^{1}H NMR)
cis/*trans* = 50/50

(6)

The hafnocene derivative **6** could also be prepared similarly, using Mg/HgCl$_2$ as reducing agents (Eq. (6)). The NMR observation showed similar signals to the Zr complex **1a**. The *cis*/*trans* ratio was 50/50 after 1 h at r.t, and the isomerization from *cis*-**6** to *trans*-**6** was significantly slower than observed for the Zr complex. It required heating at 50 °C overnight (*cis*/*trans* = 38/62). Recrystallization from hexane solution gave *trans*-**6** as colorless needle crystals that allowed us to achieve the X-ray diffraction analysis (Fig. 4). This is the first example of a 1-hafnacyclopent-3-yne compound. Judging from the space group and the similar cell parameters, it was almost isostructural to the zirconium derivative **1a**, although the C2–C3 length of 1.229(7) Å is slightly longer. The hafnacyclopentyne plane is again tilted away from the perpendicular to the Cp(centroid)–Hf–Cp(centroid) plane (86.(2)°), as observed in **1a** and **5**.

We tried to prepare the hafnium analogue of **1c** and **2** starting with 1,4-dichlorobut-2-yne (Eq. (7)). The reaction was conducted similarly to the zirconium complex **1c**. ^{1}H NMR spectroscopy showed two singlets at 5.15 and 2.54 ppm assignable to Cp and methylene protons respectively, suggesting the formation of **7** in ca. 30% yield by ^{1}H NMR. Our attempt to isolate **7**, however, has been unsuccessful.

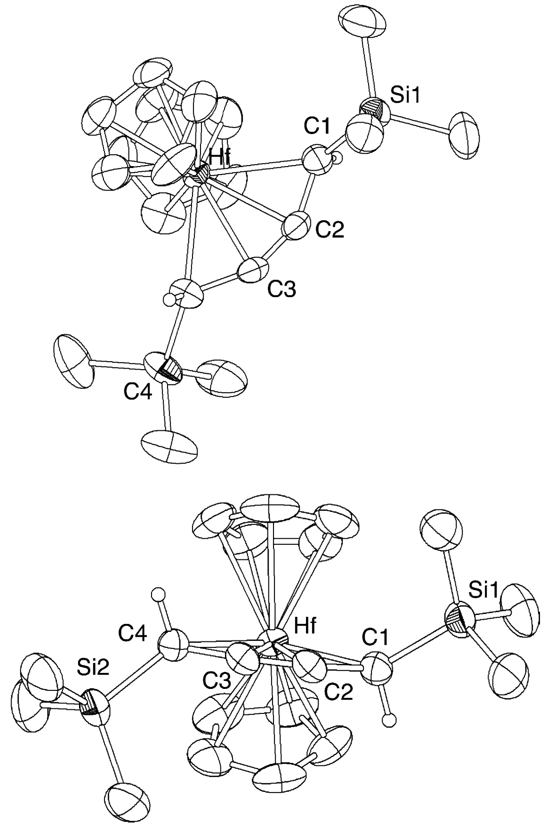
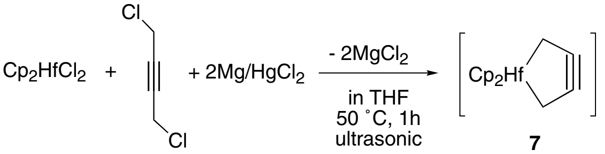


Fig. 4. The molecular structure of **6**. Drawn with 50% probability. A part of hydrogen atoms are omitted for clarity.



7

(7)

2.4. The molecular structure of Ti, Zr and Hf complexes

Bond lengths and angles of the known metallacyclopentyne compounds are summarized in Table 1 to compare the titanium, zirconium and hafnium complexes. As discussed above, the followings are noteworthy; (i) the Ti–C bonds in the metallacyclopentyne are significantly shorter than the corresponding Zr–C and Hf–C bonds; (ii) The C1–C2 bond length in the Ti complex (**2**) is slightly shorter than those in Zr and Hf complexes, whereas the C2–C2* distance in **2** is longer than those (C2–C3) in Zr and Hf; (iii) the summation of the three bond angles (excluding the C–metal bond) at C1 and C4 were 340–345° in the Zr and Hf complexes, and 350° for the Ti complex; (iv) the metallacyclopentyne plane is tilted away from perpendicular to the Cp(centroid)–metal–Cp(centroid) plane when it has large trimethylsilyl groups, whereas these two planes are vertical in non-substituted metallacyclopentynes. In addition, the lengths of C–C triple bonds are in the range1.23–1.24 Å for most cases, which is in good correspondence to the calculated results [30,31]. The facts (ii) and (iii) suggests the larger contribution of η^4-π,π-coordination mode in the titanium complex.

The selected chemical shifts in the ^1H and ^{13}C NMR spectra and coupling constants ($^1J_{CH}$) are shown in Table 2. It was found that the protons at α-carbons appeared downfield in the order Ti > Zr > Hf, while Cp signals were observed 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 in the upper magnetic field compared to the dialkyltitanocenes(IV) and zirconocenes(IV) [32–34]. Carbons attached to Ti metals are commonly observed at lower field compared with the corresponding Zr and Hf compounds [35–37]. 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. The differences in reactivity of titana-, zircona- and hafnacyclopentyne complexes are now being investigated.

3. Experimental

3.1. General

All manipulations were carried out under an argon atmosphere. Anhydrous THF and hexane were purchased from Kanto Kagaku and degassed prior to use. Dichlorobis(cyclopentadienyl)titanium, dichlorobis(cyclopentadienyl)zirconium, dichlorobis(cyclopentadienyl)hafnium and *n*-butylmagnesium chloride (1.0 M THF solution) were purchased from Kanto Kagaku. Dichlorobis(methylcyclopentadienyl)zirconium was purchased from Acros Organics and used as received. 1,4-Dichlorobut-2-yne was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**3**) was prepared according to the literature methodd [26]. ^1H and ^{13}C NMR were recorded on JEOL AL-300 and AL-400 spectrometers. Infrared spectra on TravelIR total reflection infrared spectroscopy equipment (SensIR Technologies).

Table 2
Selected ^1H and ^{13}C NMR spectroscopic data (ppm) for 1-metalalcyclopent-3-yne complexes[a]

$^1H/^{13}C$		Ti	Zr	Hf
		cis-**4**	*cis*-**1a**	*cis*-**6**
^1H	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-**4**	*trans*-**1a**	*trans*-**6**
^1H	C*H*	2.28	2.15	1.95
	C_5H_5	4.94	5.18	5.13
^{13}C	*C*H ($^1J_{CH}$)[b]	53.66 (136)	39.48 (131)	37.99 (132)
	C≡C	108.80	103.59	98.80
		2[c]	**1c**	**7**
^1H	CH_2	3.03	2.73	2.54[d]
	C_5H_5	4.68	4.99	5.15[d]
^{13}C	CH_2 ($^1J_{CH}$)[b]	51.18 (159)	38.64 (154)	nd[e]
	C≡C	106.88	102.45	nd[e]

[a] In C_6D_6.
[b] Hz.
[c] Ref. [23].
[d] In THF/C_6D_6.
[e] Not detected.

3.2. Preparation of 2

A solution of Cp_2TiCl_2 (249 mg, 1 mmol) and 1,4-dichlorobut-2-yne (184 mg, 1.5 mmol) in THF (5 mL) in the presence of dry Mg powder (73 mg, 3 mmol) was sonicated at 50 °C for 1 h. ^1H NMR observation of the dark green solution showed the formation of **2** in 60% yield. Volatiles were removed in vacuo and the residue was dissolved in hexane and filtered. The filtrate was concentrated and cooled to −20 °C. Dark brown crystals of **2** were obtained in 9% isolated yield. Spectroscopic data were identical to the literature [23].

3.3. Preparation of 4

To a solution of Cp_2TiCl_2 (1.24 g, 5 mmol) in THF (30 mL) was added *n*-butylmagnesium chloride (1.0 M THF solution, 10 mmol) and **3** (0.98 g, 5 mmol) at −78 °C. The mixture was warmed to r.t. and stirred for 1 h. ^1H NMR spectroscopy showed the formation of **4** as a mixture of *cis*- and *trans*-isomers (*cis*/*trans* = 33/67). Total yield was 76% by NMR in this stage. *cis*-**4**, ^1H NMR (C_6D_6): δ 0.13 (s, 18H), 2.49 (s, 2H), 4.86 (s, 5H), 5.03 (s, 5H). ^{13}C NMR (C_6D_6): δ −1.30, 53.44, 101.03, 103.28, 108.80. *trans*-**4**, ^1H NMR (C_6D_6): δ 0.15 (s, 18H), 2.28 (s, 2H), 4.94 (s, 10H). ^{13}C NMR (C_6D_6): δ −1.08, 53.66, 102.18, 107.96.

3.4. Preparation of 5

To a solution of $(\eta^5\text{-}C_5H_4Me)_2ZrCl_2$ (160.2 mg, 0.5 mmol) in THF (2.5 mL) was added *n*-butylmagnesium chloride (2 M in THF, 1.2 mmol) and (*Z*)-1,4-bis(trimethylsilyl)-1,2,3- butatriene (**3**; 136 mg, 0.69 mmol) at −78 °C and the mixture was warmed up to r.t. It was stirred at 50 °C for an additional 1 h. NMR observation showed the formation of 5 as a 50/50 mixture of *cis*- and *trans*-isomers; the combined yield was 89%. Then dioxane (0.3 mL) was added and stirred at r.t. for 20 min. The solution was dried and the residue was dissolved in diethyl ether. The solution was filtered and the filtrate was concentrated and cooled to −78 °C. The title compound was obtained as colorless block crystals in 55% isolated yield.

cis-**5**, ^1H NMR (C_6D_6): δ 0.30 (s, 18H), 1.39 (s, 3H), 2.05 (s, 3H), 2.12 (s, 2H), 4.85 (m, 2H), 4.96 (m, 2H), 5.12 (m, 2H), 5.66 (m, 2H). ^{13}C NMR (C_6D_6): δ 1.60, 13.33 (Me), 15.74 (Me), 38.95 (CH), 100.61 (CH), 101.49 (CH), 104.60 (q), 105.34 (CH), 108.17 (CH), 114.33 (q), 115.55 (q).

trans-**5**, ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H), 1.80 (s, 6H), 2.00 (s, 2H), 4.72 (m, 2H), 5.05 (m, 2H), 5.22 (m, 2H), 5.49 (m, 2H). ^{13}C NMR (C_6D_6): δ 1.62, 14.82 (Me), 40.41 (CH), 101.40 (CH), 102.31 (CH), 105.34 (CH), 106.54 (q), 107.60 (CH), 115.47 (q). IR (neat): 936, 1248, 1559, 2018, 2373, 2956 cm^{-1}. m.p. 180–185 °C (dec.). Elemental analysis did not give satisfactory results. The ^{13}C NMR spectra are shown in the Supplementary materials.

3.5. Preparation of Hf complex 6

Cp_2HfCl_2 (380 mg, 1 mmol) and **3** (206 mg, 1.05 mmol) were dissolved in THF (5 mL). To this solution was added dry Mg powder (29 mg, 1.2 mmol) and $HgCl_2$ (13 mg, 0.05 mmol), and the mixture was sonicated at r.t. for 1 h followed by stirring at r.t. overnight. ^{1}H NMR spectroscopy showed the formation of **6** as a mixture of *cis*/*trans* isomers (*cis*/*trans* = 50/50). Total yield was 73% by ^{1}H NMR in this stage. Recrystallization of **6** from hexane solution gave crude product as a white solid (yield 75%). Repeated recrystallization gave the title compound as colorless needle crystals in 13% yield. *cis*-**6**, ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H), 1.95 (s, 2H), 4.96 (s, 5H), 5.30 (s, 5H). ^{13}C NMR (C_6D_6): δ 1.72, 37.45, 98.27, 101.71, 103.21. *trans*-**6**, ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H), 2.02 (s, 2H), 5.13 (s, 10H). ^{13}C NMR (C_6D_6): δ 1.72, 37.99, 98.80, 102.45. IR (neat): 830, 953, 1017, 1241, 1439, 2016, 2890, 2944 cm^{-1}. m.p. 140 °C (dec.). Anal. Calc. for $C_{20}H_{30}Si_2Hf$: C, 47.56; H, 5.99. Found: C, 47.18; H, 6.03%.

3.6. Preparation of 7

To a suspension of dry Mg powder (97 mg, 4 mmol) and $HgCl_2$ (27 mg, 0.1 mmol) in THF (5 mL) was added Cp_2HfCl_2 (2387.5 mg, 1 mmol) and 1,4-dichlorobut-2-yne (246 mg, 2 mmol) at r.t. The mixture was sonicated at 50 °C for 1 h. NMR was measured using a mixture of THF and C_6D_6 as a solvent. ^{1}H NMR observation of the brownish mixture suggested the formation of **7** in about 30% yield accompanied by some unidentified products. ^{1}H NMR (THF/C_6D_6): δ 2.54 (s, 4H), 5.15 (s, 10H).

3.7. X-ray diffraction analysis of 2

Single crystals were obtained by recrystallization from a hexane solution at −20 °C. A dark brown crystal (0.5 × 0.5 × 0.2 mm) was mounted in a nylon loop and coated with liquid paraffin. Data were collected on a Rigaku

Table 3
Crystal data and structure refinement for metallacyclopentyne complexes

Complex	2	5	6
Empirical formula	$C_{14}H_{14}Ti$	$C_{22}H_{34}Si_2Zr$	$C_{20}H_{30}HfSi_2$
Formula weight	230.16	445.90	505.11
Crystal color, habit	Brown, cubic	Colorless, block	Colorless, needle
Crystal dimensions	0.50 × 0.40 × 0.20 mm	0.35 × 0.35 × 0.15 mm	0.70 × 0.10 × 0.10 mm
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Lattice type	Primitive	Primitive	Primitive
Space group	*Pbcn* (#60)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Lattice parameters			
a (Å)	10.2557(8)	7.393(1)	13.2420(2)
b (Å)	11.3683(6)	20.946(6)	12.4750(2)
c (Å)	9.4145(7)	14.571(2)	14.2090(2)
β (°)		93.289(9)	114.4850(10)
V (Å^3)	1097.6(1)	2252.6(8)	2136.15(6)
Z value	4	4	4
Absorption coefficient (cm^{-1})	7.40	5.97	6.66
Radiation	Mo Kα (λ = 0.71073 Å) Graphite monochromated	Mo Kα (λ = 0.71073 Å) Graphite monochromated	Synchrotron (λ = 0.3282 Å) Bending magnet on SPring-8 BL04B2
Temperature (K)	153	108	296
No. of reflections measured	Total: 12167 Unique: 1252 (R_{int} = 0.057)	Total: 20293 Unique: 5091 (R_{int} = 0.036)	Total: 34031 Unique: 6077 (R_{int} = 0.0367)
Corrections	Lorentz-polarization absorption (trans. factors: 0.6721–0.8624)	Lorentz-polarization	Semi-empirical from equivalents
No. of reflections	1252	5091	6077
No. variables	97	234	226
Reflection/parameter ratio	12.91	21.76	26.89
Residuals: *R*; *Rw*	0.058; 0.086	0.069; 0.105	0.0398; 0.0934
Residuals: R_1	0.033	0.041	0.0344
No. of reflections to calc. R_1	881	4019	5415
Goodness of fit indicator	0.86	1.36	1.208
Max shift/error in final cycle	0.003	0.012	0.001
Maximum peak in final diff. map (e Å^{-3})	0.32	0.88	2.368
Minimum peak in final diff. map (e Å^{-3})	−0.34	−0.55	−2.215

RAXIS-CS Imaging Plate diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K. The structure was solved by direct methods [38] and expanded using Fourier techniques [39]. Hydrogen atoms were refined isotropically. The refinements were carried out by a least-squares method on F^2. All calculations were performed using the TEXSAN software package [40]. Crystal data are summarized in Table 3. See the CIF data (CCDC-250108) for details.

3.8. X-ray crystallographic analysis of **5**

Single crystals were obtained by recrystallization from a diethyl ether solution. A colorless block crystal ($0.35 \times 0.35 \times 0.15$ mm) was mounted in a loop. Data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation at −165 °C. The structure was solved by direct methods [38] and expanded using Fourier techniques [39]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms, H1 and H4, were refined isotropically, and the rest were included in fixed positions. The refinements were carried out by a least-squares refinement on F^2. All calculation were performed using the TEXSAN software package [40]. Crystal data are summarized in Table 3. See the CIF data (CCDC-276485) for details.

3.9. X-ray diffraction analysis of **6**

A single crystal of **6** was obtained by recrystallization from hexane solution. The single crystal with dimensions of $0.7 \times 0.1 \times 0.1$ mm was sealed in a glass capillary together with Ar gas. Diffraction data were collected on an automated imaging plate Weissenberg camera, Mac-Science DIP-LABO, on the BL04B2 beam line at SPring-8 [41] using 37.8 keV (0.3282 Å) radiation with an oscillation method at room temperature. In all, 108 frames were measured with oscillation angle 3° and interval 2.5° with two different crystal orientations. Measured Bragg spots were integrated, and scaled and averaged with the programs DENZO and SCALEPACK [42], respectively. Lorentz, polarization and absorption corrections were applied. Measured and independent reflections, and completeness were 34031, 6077, and 0.981, respectively. The structure was solved by a direct method and refined with the program SIR97 [38] and SHELXL97 [43], respectively. Crystal data are summarized in Table 3. See the CIF data (CCDC-276486) for details.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.052.

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