Synthesis and Structure of 1-Titana- and 1-Hafnacyclopent-3-yne Complexes[1]

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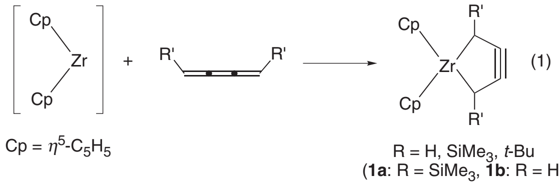
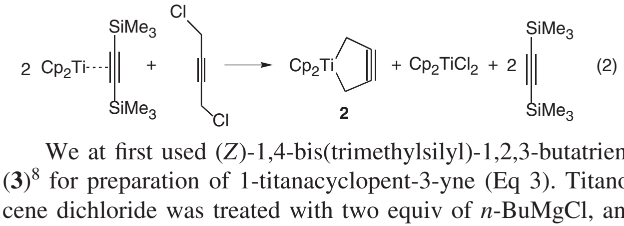
1-Titanacyclopent-3-yne and 1-hafnacyclopent-3-yne complexes were synthesized, and one of the titanium compounds was structurally characterized. Its molecular structure was similar to the zirconium analogue, although shorter Ti–C bonds may emphasize the ring strain of the five-membered cyclic alkyne structure.

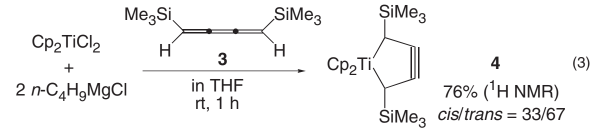
Small cyclic alkynes are usually unstable and difficult to isolate.[2] We recently reported the synthesis and structure of 1-zirconacyclopent-3-yne complexes that can be regarded as the first isolable five-membered cyclic alkynes (Eq 1).[3] We also reported a simple and versatile preparative method for zirconacyclopentyne, that is derived from Cp_2ZrCl_2 and 1,4-dichloro-2-butyne.[4] Five-membered metallacyclocumulenes reported by Rosenthal and co-workers have similar structure and reactivity to metallacyclopentynes.[5] They have prepared a variety of zirconacyclocumulenes as well as titanacyclocumulenes and extensively studied their reactivity, although, to the best of our knowledge, a hafnium analogue has not been reported. They demonstrated that these zirconium and titanium complexes showed a few slight differences in their molecular structures.[6]



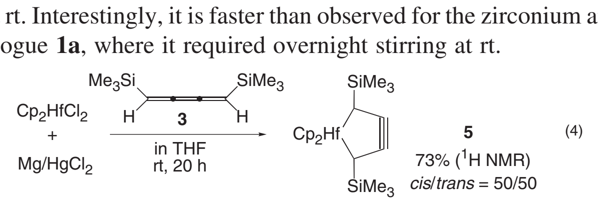
For metallacyclopentyne complexes, to compare the structure of zirconium and titanium complexes is important in understanding their property. Thus we subsequently aimed to synthesize metallacyclopentynes of other group 4 metals. During the course of our study, very recently Rosenthal and co-workers have reported preparation of a 1-titanacyclopent-3-yne compound **2** using modification of our method, although the molecular structure of **2** was not shown (Eq 2).[7] We wish to report here our results, the synthesis and structure of 1-titanacyclopent-3-yne and 1-hafnacyclopent-3-yne complexes.[1]



We at first used (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene (**3**)[8] for preparation of 1-titanacyclopent-3-yne (Eq 3). Titanocene dichloride was treated with two equiv of *n*-BuMgCl, and then reacted with **3**.[9] NMR observation of the reaction mixture indicated the formation of 1-tianacyclopent-3-yne **4** as a mixture of *cis*- and *trans*-isomers.

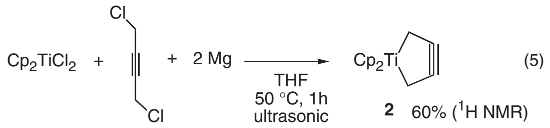


Cyclopentadienyl (Cp) rings appeared at 4.86 and 5.03 ppm for the *cis*-isomer and 4.94 ppm for the *trans*-isomer. The methine protons were observed at 2.49 and 2.28 ppm for *cis*- and *trans*-isomers, respectively. In ^{13}C NMR spectrum, signals assignable to quaternary alkynyl carbons in *cis*- and *trans*-isomers were observed at 107.96 and 108.80 ppm, respectively. These spectra are similar to those of the corresponding zirconium analogue,[3] supporting the formation of **4**. The isomerization from the *cis*-isomer to the *trans* reached to an equilibrium after 1 h at rt. Interestingly, it is faster than observed for the zirconium analogue **1a**, where it required overnight stirring at rt.

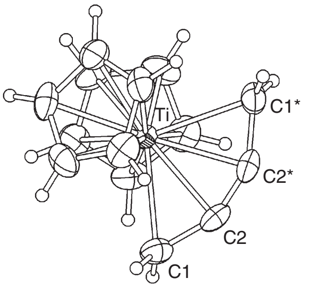


The hafnocene derivative **5** could be also prepared similarly using Mg/$HgCl_2$ as reducing agents (Eq 4).[10] The NMR observation showed similar signals to the Zr complex (vide infra). The *cis*/*trans* ratio was 50/50 after 1 h at rt, and the isomerization from *cis*- to *trans*-**5** was significantly slower than observed for the Zr complex **1a**. It required heating at 50 °C overnight (*cis*/*trans* = 38/62). It is noteworthy that this is the first example of 1-hafnacyclopent-3-yne compound. However, attempts to isolate these Ti and Hf complexes in a pure form have been unsuccessful so far.[11]

Then we applied the method starting from 1,4-dichloro-2-butyne to titanium. The procedure was similar to the preparation of the zirconium derivative **1b** (Eq 5).[12]



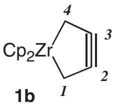
Titanacyclopent-3-yne compound **2** was formed in 60% yield by ^{1}H NMR. Recrystallization from hexane solution gave dark brown crystals of **2** despite low yield (9%). Spectroscopic data were identical to the reported results.[7a] The molecular structure of **2** was determined by X-ray diffraction study (Figure 1). This is the first example of structurally characterized 1-titanacyclopent-3-yne. Its structure is similar to that of the zirconium analogue **1b** (Figure 2).[13] Four carbons of butatriene and Ti metal are coplanar, and the butatriene moiety is bent to form a strained five-membered metallacycle. The C1–C2 and C2–C2* bond lengths are in a similar range to those of **1b**, as well as the C1–C2–C2* angle. On the other hand, the Ti–C1 and Ti–C2 distances are significantly shorter than the Zr–C1/C4 and Zr–C2/C3 distances of **1b**. Although shorter Ti–C bonds compared to the corresponding Zr–C bonds are usually observed,[14] these results imply a more strained structure of **2** than that of **1b**. This led us to examine the NMR data of the metallacyclpentynes complexes.



Selected bond lengths (Å) and angles (deg)

C1–C2	1.393(3)
C2–C2*	1.248(4)
Ti–C1	2.353(2)
Ti–C2	2.202(2)
Ti–C1–C2	66.4(1)
C1–Ti–C1*	103.8(1)
C1–C2–C2*	151.7(1)

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



1b

C1–C2	1.406(4)	Zr–C1	2.415(3)	C1–C2–C3	151.5(3)
C3–C4	1.408(5)	Zr–C4	2.428(3)	C2–C3–C4	151.3(3)
C2–C3	1.237(5)	Zr–C2	2.314(3)	Zr–C1–C2	68.8(2)
		Zr–C3	2.320(3)	C1–Zr–C4	99.9(1)

Figure 2. Selected bond distances (Å) and angles (deg) of **1b**.

Selected data of chemical shifts for Ti, Zr, and Hf complexes are summarized in Table 1. In both ^{1}H and ^{13}C NMR, the signals due to Me_3Si and Cp groups appeared in similar regions regardless of the metals, while those assigned to butatriene appeared downfield in the order Ti > Zr > Hf. Particularly ^{13}C signals for α-carbons (*C*H or *C*H_2) in the Ti complexes at 51–53 ppm were much downfield compared to those in the Zr and Hf complexes.

Table 1. Chemical shifts (ppm) in ^{1}H and ^{13}C NMR for 1-metalalcyclopent-3-yne complexes[a]

^{1}H/^{13}C		Ti	Zr	Hf
		cis-**4**	*cis*-**1a**	*cis*-**5**
^{1}H	C*H*	2.49	2.19	2.02
^{13}C	*C*H	53.44	38.91	37.45
	C≡C	107.96	102.92	98.27
		trans-**4**	*trans*-**1a**	*trans*-**5**
^{1}H	C*H*	2.28	2.15	1.95
^{13}C	*C*H	53.66	39.48	37.99
	C≡C	108.80	103.59	98.80
		2	**1b**	
^{1}H	CH_2	3.03	2.73	
^{13}C	*C*H_2	51.18	38.64	
	C≡C	106.88	102.45	

[a] in C_6D_6.

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References and Notes

1 A part of this work (preparation of **4** and **5**) was previously presented. 49th Symposium on Organometallic Chemistry, Kobe, September. 2002.

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9 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 rt and stirred for 1 h. ^{1}H NMR spectroscopy showed the formation of **4** as a mixture of *cis*- and *trans*-isomers ($c/t = 33/67$). Total yield was 76% by NMR in this stage. *cis*-**4**, ^{1}H 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, 107.96. *trans*-**4**, ^{1}H 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, 108.80.

10 THF (5 mL) was added to dry Mg powder (29 mg, 1.2 mmol) and $HgCl_2$ (13 mg, 0.05 mmol). Cp_2HfCl_2 (380 mg, 1 mmol) and **3** (206 mg, 1.05 mmol) were dissolved in the solution, and the mixture was sonicated at rt for 1 h followed by stirring at rt overnight. ^{1}H NMR spectroscopy showed the formation of **5** as a mixture of *cis*/*trans* isomers ($c/t = 50/50$). Total yield was 73% by ^{1}H NMR in this stage. *cis*-**5**, ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H), 2.02 (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*-**5**, ^{1}H NMR (C_6D_6): δ 0.28 (s, 18H), 1.95 (s, 2H), 5.13 (s, 10H). ^{13}C NMR (C_6D_6): δ 1.72, 37.99, 98.80, 102.45.

11 Recrystallization of **5** from hexane solution gave crude product as white solid ($c/t = 3/97$, 8% crude) that was considerably pure based on NMR and elemental analysis, while **4** transformed to unidentified species during the operation.

12 A solution of Cp_2TiCl_2 (249 mg, 1 mmol) and 1,4-dichloro-2-butyne (191 mg, 1.55 mmol) in THF (5 mL) in the presence of dry Mg powder (73 mg, 3 mmol) was sonicated at 50 °C for 1 h. ^{1}H 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 at −20 °C. Dark brown crystals of **2** were obtained in 9% isolated yield. Crystallographic Data: $C_{14}H_{14}Ti$, FW = 230.16, orthorhombic, *Pbcn* (No. 60), $a = 10.2557(8)$, $b = 11.3683(6)$, $c = 9.4145(7)$ Å, $V = 1097.6(1)$ Å^3, $Z = 4$, $R_1 = 0.033$, $R_w = 0.086$, GOF = 0.86 (CCDC- 250108).

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14 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). a) Ti: U. Thewalt and T. Wöhrle, *J. Organomet. Chem.*, **464**, C17 (1994). b) Zr: W. E. Hunter, D. C. Hrncir, R. V. Bynum, R. A. Penttila, and J. L. Atwood, *Organometallics*, **2**, 750 (1983).

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