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Reaction Mechanisms |*Hot Paper*|

Direct Evidence for a [4+2] Cycloaddition Mechanism of Alkynes to Tantallacyclopentadiene on Dinuclear Tantalum Complexes as a Model of Alkyne Cyclotrimerization

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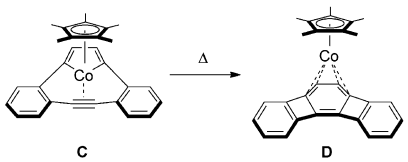
Abstract: A dinuclear tantalum complex, $[Ta_2Cl_6(\mu\text{-}C_4Et_4)]$ (**2**), bearing a tantallacyclopentadiene moiety, was synthesized by treating $[(\eta^2\text{-}EtC{\equiv}CEt)TaCl_3(DME)]$ (**1**) with $AlCl_3$. Complex **2** and its Lewis base adducts, $[Ta_2Cl_6(\mu\text{-}C_4Et_4)L]$ (L = THF (**3a**), pyridine (**3b**), THT (**3c**)), served as more active catalysts for cyclotrimerization of internal alkynes than **1**. During the reaction of **3a** with 3-hexyne, we isolated $[Ta_2Cl_4(\mu\text{-}\eta^4{:}\eta^4\text{-}C_6Et_6)(\mu\text{-}\eta^2{:}\eta^2\text{-}EtC{\equiv}CEt)]$ (**4**), sandwiched by a two-electron reduced $\mu\text{-}\eta^4{:}\eta^4$-hexaethylbenzene and a $\mu\text{-}\eta^2{:}\eta^2$-3-hexyne ligand, as a product of an intermolecular cyclization between the metallacyclopentadiene moiety and 3-hexyne. The formation of arene complexes $[Ta_2Cl_4(\mu\text{-}\eta^4{:}\eta^4\text{-}C_6Et_4Me_2)(\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**7b**) and $[Ta_2Cl_4(\mu\text{-}\eta^4{:}\eta^4\text{-}C_6Et_4RH)(\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (R = *n*Bu (**8a**), *p*-tolyl (**8b**)) by treating $[Ta_2Cl_4(\mu\text{-}C_4Et_4)(\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**6**) with 2-butyne, 1-hexyne, and *p*-tolylacetylene without any isomers, at room temperature or low temperature were key for clarifying the [4+2] cycloaddition mechanism because of the restricted rotation behavior of the two-electron reduced arene ligands without dissociation from the dinuclear tantalum center.

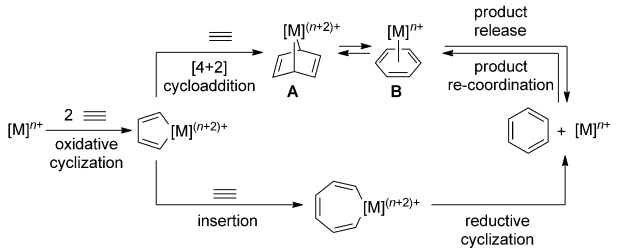
Introduction

Cyclotrimerization of alkynes assisted by various transition metal catalysts is a straightforward synthetic method for constructing substituted aromatic compounds.[1] A well-established reaction mechanism involves the oxidative coupling of two alkynes at a low-valent metal center, giving a metallacyclopentadiene, followed by further addition of an alkyne to produce the corresponding benzene derivatives (Scheme 1). Many metallacyclopentadienes of a wide variety of transition metals have been isolated, some of which act as catalysts for alkyne cyclotrimerization.[2] Although metallacyclopentadienes have been established as key intermediates for the construction of aromatic rings through [4+2] cycloaddition[3] or insertion/reductive cyclization,[4] as representatively shown in Scheme 1, the actual C–C bond-forming process has rarely been manifested. One reliable mechanism is that a metallacyclopentadiene undergoes a [4+2] cycloaddition with an incoming alkyne to give a metallanorbonadiene (**A**) or a π-arene complex (**B**). Aubert et al. investigated in detail the reaction pathway of [2+2+2] alkyne trimerization catalyzed by $[CpCoL_2]$ (L = CO, PR_3, alkenes) based on DFT calculations, in which [4+2] cycloaddition of a cobaltacyclopentadiene and an alkyne was the key reaction step for constructing the aromatic ring.[5] Direct experimental evidence for the involvement of the [4+2] cycloaddition pathway in alkyne cyclotrimerization is, however, limited to the intramolecular case; Vollhardt et al. experimentally demonstrated an intramolecular [4+2] cycloaddition of cobaltcyclopentadiene moiety in **C** with an internal coordinated C≡C bond, giving η^4-arene complex **D** [Eq. (1)]:[6]



(1)

Clear observation of the [4+2] cycloaddition pathway in intermolecular alkyne trimerization is rather complicated. Wigley et al. reported that tantalum complex **E** reacted with alkynes to give tantallanorbonadiene **F** [Eq. (2)], which acted as a catalyst for *tert*-butylacetylene cyclotrimerization. Even after form-



Scheme 1. Proposed reaction mechanism of [2+2+2] alkyne cyclotrimerization by transition metal complexes.

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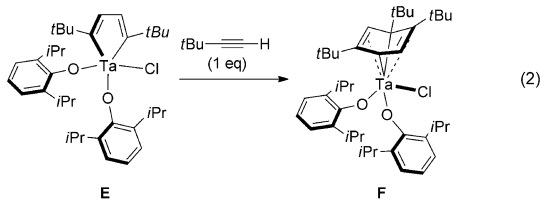
ing an arene ring through insertion/reductive cyclization pathway, recoordination of the arene ring to the low-valent metal center leads to the formation of **F**. Bergman et al. first undertook a kinetic study on the intermolecular [4+2] cycloaddition mechanism for [$CpCo(C_4Me_4)(PR_3)$] complexes;[3] however, detection of a [4+2] cycloaddition product just after the [4+2] cycloaddition has never been achieved.

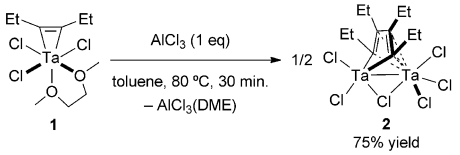


(2)

Herein, we report the synthesis of dinuclear tantalum complexes bearing arene ligands by the reaction of a dinuclear tantalum metallacyclopentadiene complex, [$Ta_2Cl_4(\mu\text{-}C_4Et_4)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$] (**6**), with several alkynes. We have obtained evidence for an intermolecular [4+2] cycloaddition pathway: the restricted rotational manner of strongly coordinating arenes without dissociation from the metal center is an important factor that determines the [4+2] cycloaddition mechanism.

Results and Discussion

Reaction of [(η^2-EtC≡CEt)$TaCl_3$(DME)] (**1**)[7] with anhydrous $AlCl_3$ (1 equiv) in toluene afforded dinuclear complex **2** as a dark-purple solid in 75% yield, along with the formation of $AlCl_3$(DME), in which anhydrous $AlCl_3$ functioned to capture DME [Eq. (3)]. The molecular structure of **2** was characterized spectroscopically, and further established by an X-ray diffraction study (Figure 1 and Table 1), which clearly indicated the formation of a dimetallacyclopentadiene structure bridging two tantalum atoms. The distances of Ta1–C1 (2.031(14) Å) and Ta1–C4 (2.011(14) Å) in the tantallacyclopentadiene unit are shorter than those of [Ta(CEt=CEtCEt=CEt)(DIPP)$_3$] (DIPP = 2,6-diisopropylphenoxy).[8] Coordination of the tantallacyclopentadiene moiety to the second tantalum atom results in deformation of the planar metallacyclopentadienyl moiety with a fold angle of 44.4° between the C1-Ta1-C4 and C1-C2-C3-C4 planes. Reports of halide cluster complexes of Nb and W bearing a metallacyclopentadiene unit are rare,[9] although there are many homo- or hetero-multinuclear transition metal carbonyl complexes of Cr, Mo, W, Os, Fe, Ru, and Co containing a metallacyclopentadiene moiety.[10]



(3)

Lewis bases such as tetrahydrofuran (THF), pyridine, and tetrahydrothiophene (THT), coordinate to the tantalum center of **2** to give the corresponding adducts **3a–c** [Eq. (4)], the molecular formulas of which were determined to contain one Lewis base, based on their spectroscopic data as well as on the molecular structure of **3a** by an X-ray diffraction study (Figure 1 and Table 1). In contrast to the deformed planarity of **2**, the tantallacyclopentadiene moiety of **3a** is almost planar, as evident from the angle (7.2°) between the C1-Ta1-C4 and C1-C2-C3-C4 planes.

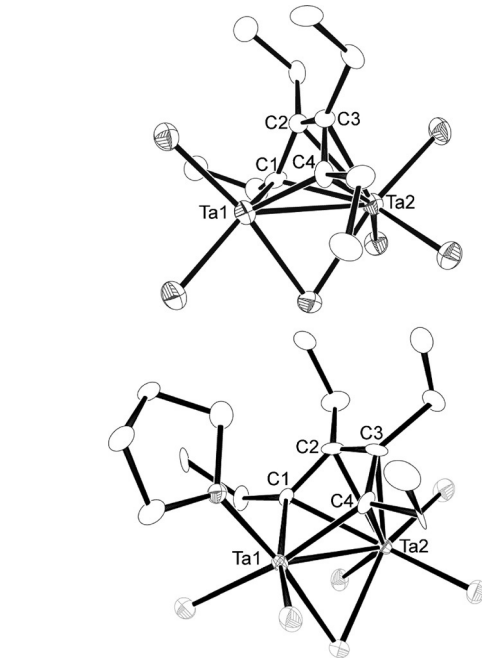
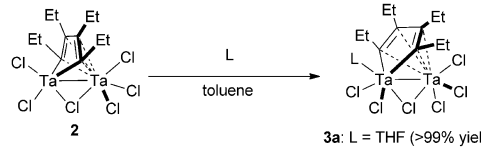


Figure 1. Molecular structures of dinuclear tantalum complexes **2** (top) and **3a** (bottom) with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) of complexes **2** and **3a**.

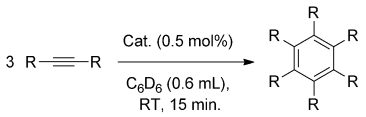
	2	**3a**
Ta1–Ta2	3.011(2)	2.9877(4)
Ta1–C1	2.031(14)	2.173(6)
Ta1–C4	2.011(14)	2.157(6)
Ta2–C1	2.319(13)	2.426(6)
Ta2–C2	2.446(13)	2.424(5)
Ta2–C3	2.426(13)	2.409(6)
Ta2–C4	2.341(18)	2.421(6)
C1–C2	1.442(19)	1.418(9)
C2–C3	1.43(2)	1.448(9)
C3–C4	1.44(2)	1.439(8)
dihedral angle between C1-Ta1-C4 and C1-C2-C3-C4 planes	44.4	7.2



(4)

The mononuclear and dinuclear tantalum complexes **1**, **2**, and **3a–c** function as catalysts for the cyclotrimerization reaction of internal alkynes (Table 2). Under ambient conditions in [D_6]benzene, complex **2** (0.5 mol%) converted 3-hexyne quantitatively into hexaethylbenzene within 15 min (Table 2, entry 2), whereas complex **1** exhibited very low catalytic activity (entry 1). Complexes **3a–c** showed less catalytic activity than complex **2** due to coordination of the donor ligands to the dinuclear tantalum core (Table 2, entries 3–5). Internal alkynes such as 2-butyne and 4-octyne were also trimerized by complex **2** to give the corresponding hexaalkylbenzene in quantitative yield (Table 2, entries 6 and 7).

Table 2. Catalytic trimerization of internal alkynes by tantalum complexes **1**, **2**, and **3a–c**.

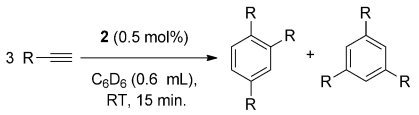


Entry	Cat.	R	Yield [%][a]
1	**1**[b]	Et	7
2	**2**	Et	>99
3	**3a**	Et	47
4	**3b**	Et	22
5	**3c**	Et	94
6	**2**	Me	>99
7	**2**	*n*Pr	>99

[a] Determined by ^{1}H NMR spectroscopic analysis. [b] 1 mol% of **1** was used.

Terminal alkynes such as 1-hexyne and *p*-tolylacetylene were trimerized by **2** to produce a mixture of trisubstituted benzene derivatives in quantitative yield (Table 3).

Table 3. Catalytic trimerization of terminal alkynes by complex **2**.

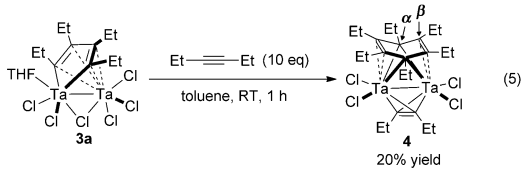


Entry	R	Yield [%][a]	1,2,4/1,3,5[a]
1	*n*Bu	>99	72:28
2	*p*-tolyl	>99	64:36

[a] Determined by ^{1}H NMR spectroscopic analysis.

To detect species present during the cyclotrimerization, we conducted the reaction of **3a** with 3-hexyne (10 equiv), from which we isolated the new dinuclear tantalum complex **4** in 20% yield [Eq. (5)]. Notably, the main motif of complex **4** was a unique sandwich structure, in which the dinuclear tantalum center was sandwiched by a two-electron reduced μ-η^4:η^4-hexaethylbenzene ligand and by a μ-η^2:η^2-3-hexyne ligand, based on the ^{1}H and ^{13}C NMR spectral data. In the ^{13}C NMR spectrum, two resonances assignable to ring carbon atoms of C_6Et_6, denoted as Cα and Cβ, were observed: signals due to Cα and Cβ appeared at δ_C = 104.5 and 108.7 ppm, respectively, suggesting that rotation of the C_6Et_6 ligand on the dinuclear tantalum center was prevented. In contrast, fast rotation of the arene ligands on tantalum and dinuclear vanadium centers were observed for previously reported [(η^6-arene)Ta(OAr)$_3$] and [(μ-η^4:η^4-C_6H_6)(CpV)$_2$(μ-H)$_2$] complexes.[11] The ^{1}H NMR spectrum displayed resonances for two magnetically inequivalent ethyl groups of the C_6Et_6 ligand: one due to the ethyl group bound to the Cα was a quartet at δ_H = 0.72 ppm [^3J(H,H) = 7.5 Hz, CH_2CH_3] and a triplet at δ_H = 0.39 ppm [^3J(H,H) = 7.5 Hz, CH_2CH_3], and the second due to the ethyl group bound to Cβ appeared at δ_H = 2.19 and 2.77 ppm [dq, ^2J(H,H) = 14.8 Hz, ^3J(H,H) = 7.4 Hz, $CHHCH_3$] and δ_H = 1.07 ppm [t, ^3J(H,H) = 7.4 Hz, CH_2CH_3]. The upfield shift of the methylene protons bound to Cα compared with that of Cβ indicated the sp^3 carbon character of Cα. The μ-η^2:η^2-3-hexyne moiety was characterized as a dianionic alkyne ligation bridging two tantalum centers because ^{1}H NMR signals due to ethyl groups resonated at lower magnetic field at δ_H = 3.98 ppm [q, ^3J(H,H) = 7.4 Hz, CH_2CH_3] and δ_H = 1.53 ppm [t, ^3J(H,H) = 7.4 Hz, CH_2CH_3].[7,12] Although the mechanism of the reaction shown in Eq. (5) is unclear, we presume disproportionation of chloride ligands take place during the formation of complex **4**.[13]

Figure 2 and Table 4 show the molecular structure and selected geometrical parameters of **4**. The Ta1—Ta2 distance of



(5)

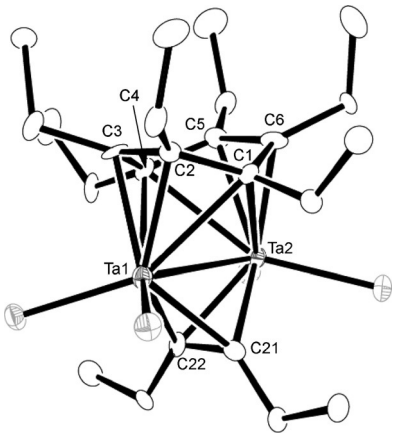


Figure 2. Molecular structure of **4** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) of complex **4**.

Ta1—Ta2	2.8737(8)	C4—C5	1.494(16)
C1—C2	1.475(18)	C5—C6	1.434(18)
C2—C3	1.407(18)	C6—C1	1.465(17)
C3—C4	1.460(16)	C21—C22	1.391(18)
dihedral angle between C1-C2-C3-C4 and C1-C6-C5-C4 planes			37.5

2.8737(8) Å is typical for a Ta^{IV}–Ta^{IV} single bond.[14] Four C–C bonds of the hexaethylbenzene ring, C1–C2, C3–C4, C4–C5, and C1–C6, are significantly elongated compared with a normal C–C bond length of aromatic compounds, indicating a 2,5-cyclohexadien-1,4-yl structure for the two-electron reduced hexaethylbenzene.[15] In addition, the bending structure of the C_6Et_6 ligand is ascertained by the dihedral angle (37.5°) between the C1-C2-C3-C4 and C1-C6-C5-C4 planes, the value of which is less acute than that of $[(C_6Et_6)Ta(DIPP)_2Cl]$ (34.4°).[11a] The bond length of C21–C22 (1.391(18) Å) in **4** is typical for a dianionic η^2-alkyne ligand found in mononuclear complexes, $[(\eta^2\text{-3-hexyne})TaCl_3(L)_2]$ (L = py; L_2 = DME, TMEDA).[7,12b]

Complex **4** was alternatively prepared by reducing **2** by using 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me_4-BTDP), which has a unique reducing ability that does not lead to the formation of any reductant-derived metal salts.[16] Treatment of complex **2** with Me_4-BTDP, followed by the addition of 3-hexyne (2 equiv) resulted in the formation of **4** in 70% yield, along with 2,3,5,6-tetramethylpyrazine (1 equiv re. **2**) and $ClSiMe_3$ (2 equiv to **2**), both of which were readily removed (Scheme 2). When Me_4-BTDP was used in the absence of alkynes, a yellow powder $[Ta_2Cl_4(\mu\text{-}C_4Et_4)]_n$ (**5**) precipitated quantitatively. This protocol for preparing **5** allowed us to introduce bis(trimethylsilyl)acetylene to give $\mu\text{-}\eta^2\text{:}\eta^2$-{bis(trimethylsilyl)acetylene} derivative **6** in 64% yield, but no cyclization with the tantallacyclopentadiene moiety proceeded due to the steric bulk of bis(trimethylsilyl)acetylene (Figure 3 and Table 5).

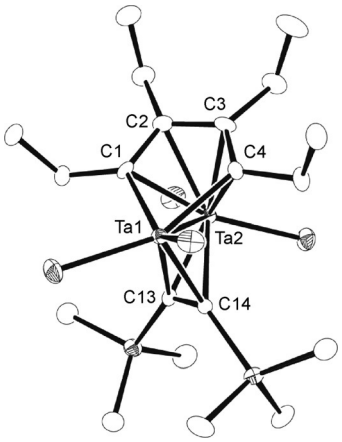
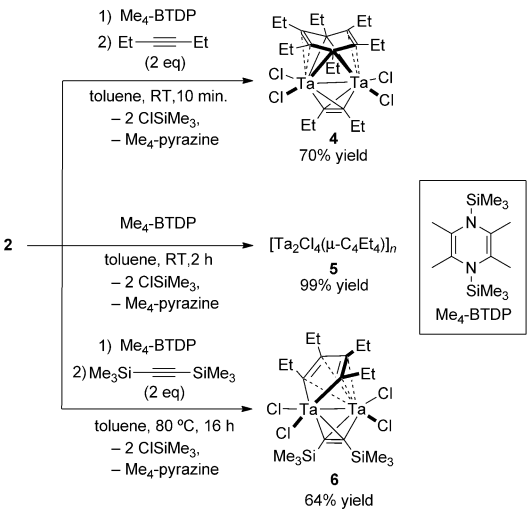


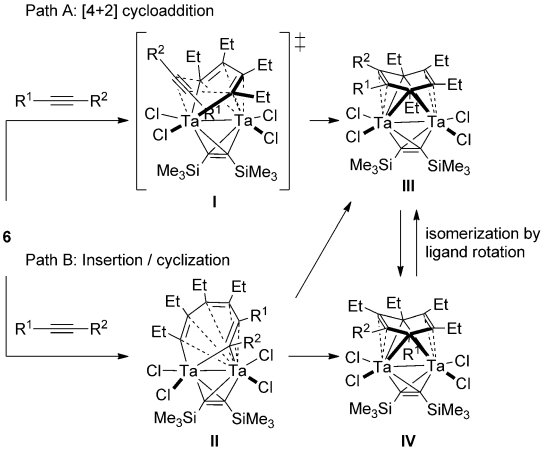
Figure 3. Molecular structure of complex **6** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 5. Selected bond lengths (Å) and angles (°) of complex **6**.

Ta1–Ta2	2.8403(4)	Ta2–C4	2.427(6)
Ta1–C1	2.172(5)	C1–C2	1.409(8)
Ta1–C4	2.183(6)	C2–C3	1.466(9)
Ta2–C1	2.389(6)	C3–C4	1.422(8)
Ta2–C2	2.387(6)	C13–C14	1.393(8)
Ta2–C3	2.359(5)		
dihedral angle between C1-Ta1-C4 and C1-C2-C3-C4 planes			0.95



Scheme 2. Reaction of complex **2** with Me_4-BTDP followed by addition of 3-hexyne or bis(trimethylsilyl)acetylene.

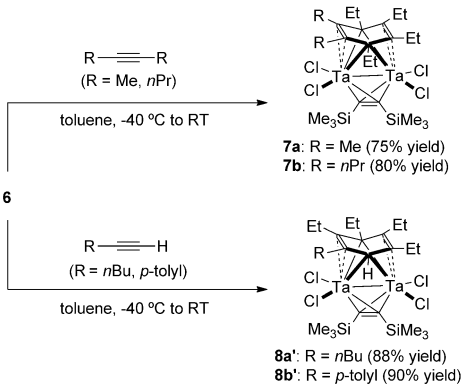


Scheme 3. Proposed mechanism of a cyclization reaction between the metallacyclopentadiene moiety of **6** and an alkyne.

With complex **6** in hand, we conducted control experiments to investigate the reaction mechanism for the formation of an arene ligand on the dinuclear tantalum center. As outlined in Scheme 3, there are two reasonable pathways for the intermolecular cyclization: one is a [4+2] cycloaddition pathway via transition state **I**, resulting in the exclusive formation of **III** just after the formation of the arene ligand (Path A), and the other is an insertion/cyclization pathway via metallacycloheptatriene intermediate **II**, giving a mixture of two isomers **III** and **IV** (Path B). When the formed arene ligand freely rotates on the dinuclear tantalum center, the final product contains both isomers, **III** and **IV**, and then the thermodynamically favored complex is formed as a single species.

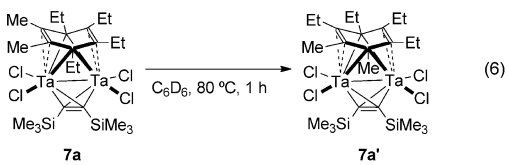
When internal alkynes, such as 2-butyne and 4-octyne, were added to **6**, C_s-symmetric complexes **7a** and **7b**, corresponding to **III** in Scheme 3, were isolated as a single product in good yield in each case (Scheme 4 and Figure 4, top, for mo-

lecular structure of **7b**; Table 6 for bond lengths and angles). When terminal alkynes, such as 1-hexyne and *p*-tolylacetylene, were adapted to this arene formation reaction, complexes **8a′** and **8b′**, corresponding to **IV**, were obtained as a single product in good yield in each case.



Scheme 4. Reactions of complex **6** with several alkynes.

Isomeric rotations of the formed arene ligands were clearly observed by variable-temperature ^{1}H NMR measurements. Heating **7a** at 80 °C in C_6D_6 solution induced rotation of the $C_6Et_4Me_2$ ligand by 60° to afford C_1-symmetric complex **7a′** as another single product [Eq. (6), Figure 4, bottom, and Table 6], which indicated that **7a′** is thermodynamically favored over **7a** due to the location of a less bulky Me group at the α-position. Rotation of the arene ligands led to the less bulky H being located at the α-position. Complexes **8a** and **8b** were detected by ^{1}H NMR measurements at −10 °C (for **8a**) or −60 °C (for **8b**) as a single product, in which singlet olefin protons due to C_6Et_4RH (δ_H = 5.53 ppm for **8a** and 6.04 ppm for **8b**) were observed in each case [Eq. (7), and the Supporting Information, Figures S1 and S2]. The isomeric rotation of the C_6Et_4RH ligands proceeded at room temperature to produce complexes **8a′** and **8b′**, which was clearly confirmed by the disappearance of the olefin protons and by the appearance of the aliphatic protons (δ_H = 1.15 ppm for **8a′** and 1.56 ppm for **8b′**). These results definitively showed that the reaction of the metallacyclopentadiene moiety of **6** with 2-butyne, 1-hexyne, and *p*-tolylacetylene proceeded through intermolecular [4+2] cy-



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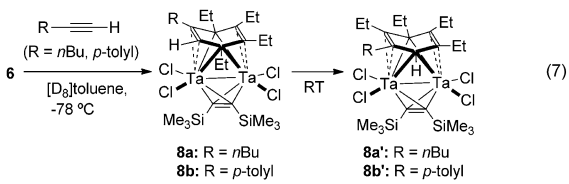

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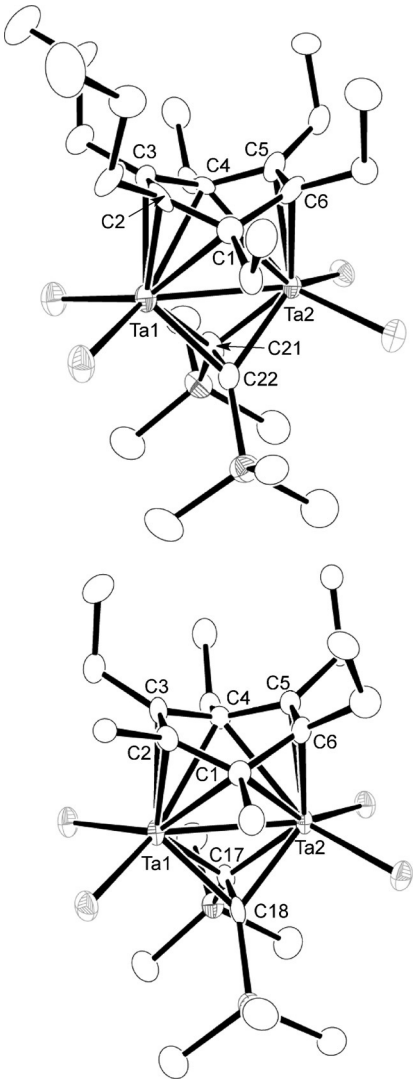

Figure 4. Molecular structures of dinuclear tantalum complexes **7b** (top) and **7a′** (bottom) with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

Table 6. Selected bond lengths (Å) and angles (°) of complexes **7b** and **7a′**.

	7b	**7a′**
Ta1–Ta2	2.8451(6)	2.8557(3)
C1–C2	1.418(13)	1.472(7)
C2–C3	1.398(13)	1.399(8)
C3–C4	1.493(12)	1.481(7)
C4–C5	1.457(13)	1.489(7)
C5–C6	1.418(13)	1.391(7)
C6–C1	1.539(14)	1.482(7)
C21–C22 (for **7b**) C17–C18 (for **7a′**)	1.443(14)	1.446(7)
dihedral angle between C1-C2-C3-C4 and C1-C6-C5-C4 planes	42.44	43.24

cloaddition (Path A). In contrast, a similar rotational behavior of the arene ligand for **7b** was not observed at high temperature, probably due to the location of the smaller Et group at the α-position. We could not rule out the involvement of

Path B and isomeric rotation of the $C_6Et_4nPr_2$ ligand in the reaction of **6** with 4-octyne to form **7b**.

Rate constants for the isomeric rotation of the $C_6Et_4Me_2$ ligand at several temperatures were measured by ^{1}H NMR spectroscopy (Figure 5, top), and the activation parameters ($\Delta G_{303K}^{\neq} = 103.8(\pm 4.4)$ kJ mol^{-1}, $\Delta H^{\neq} = 102.6(\pm 2.3)$ kJ mol^{-1}, $\Delta S^{\neq} = -3.9(\pm 6.9)$ J K^{-1} mol^{-1}) were estimated by using Eyring plots (Figure 5, bottom). Such a negative $\Delta S^{\neq}$ value indicated that the dissociation mechanism during the rotation could be ruled out.

These isolated arene dinuclear complexes were inactive for catalytic cyclotrimerization of alkynes, presumably due to the nonlability of the arene ligand and the μ-η^2:η^2-alkyne ligand. We tested the oxidation of the dinuclear tantalum center in an attempt to release the arene ligands. The C_6Et_6 ligand of **4** was quantitatively released upon the addition of oxidants such as 2,6-lutidine *N*-oxide, WCl_6, and AgBArF (BArF = B{3,5-$(CF_3)_2C_6H_3$}$_4$). It is assumed that the catalytically active species in the cyclotrimerization reaction contains a {Ta_2Cl_6} fragment for releasing arenes as reaction products.

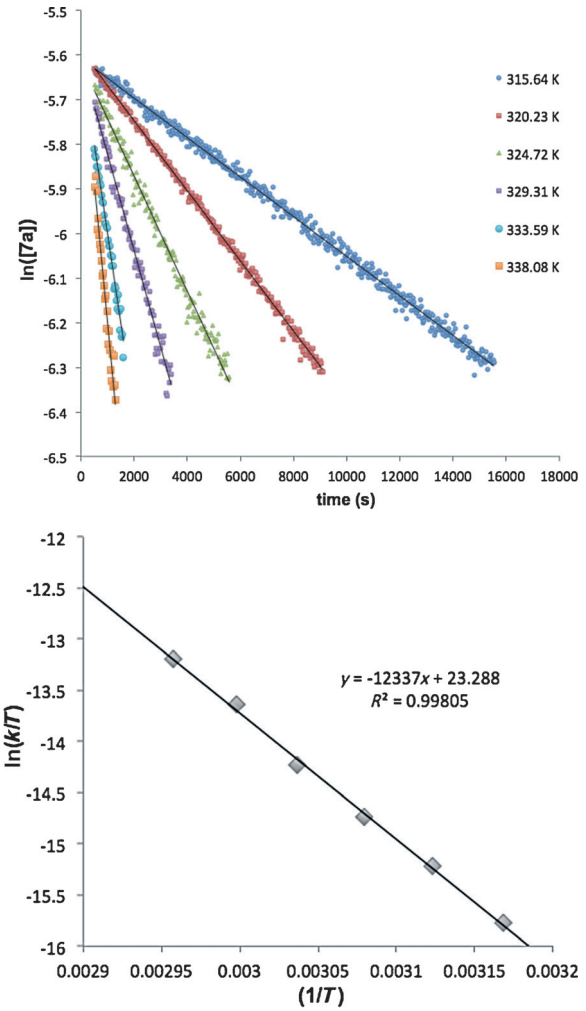

Figure 5. Representative plot of ln([**7a**]) versus time (top) and Eyring plots (bottom) for conversion of **7a** into **7a′**. First-order rate constants were determined by monitoring the decay of **7a** by ^{1}H NMR spectroscopy. *k* (10^{-4} mol s^{-1}) = 0.4440 (315.64 K), 0.7866 (320.23 K), 1.288 (324.72 K), 2.162 (329.31 K), 3.991 (333.59 K), 6.264 (338.08 K).

Conclusion

We have synthesized several dinuclear tantalum complexes bearing μ-η^4:η^4-arene and μ-η^2:η^2-alkyne ligands from tantallacyclopentadiene complexes. The formation of complexes **7a**, **8a**, and **8b** by the reaction of **6** with the corresponding alkynes confirmed the intermolecular [4+2] cycloaddition of the tantallacyclopentadiene moiety with an external alkyne. The restricted rotational behavior of the arene ligands on the dinuclear tantalum center enabled us to isolate **7a** at room temperature and to detect **8a** and **8b** at low temperature just after the intermolecular [4+2] cycloaddition reaction. In this context, our system represents a model for the catalytic intermolecular alkyne trimerization. Further investigation of dinuclear complexes of group 5 metals as catalysts is ongoing in our laboratory.

Experimental Section

General

All manipulations involving air- and moisture-sensitive tantalum complexes were performed either under argon by using standard Schlenk techniques or in an argon-filled glovebox. [(η^2-EtC≡CEt)-$TaCl_3$(DME)] (**1**)[7] and 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (Me_4-BTDP)[16] were prepared according to reported procedures. Alkynes were purchased from TCI or Aldrich and distilled over CaH_2 before use. Anhydrous hexane, toluene, and THF were purchased from Kanto Chemical, and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[17] Benzene, [D_6]benzene, [D_8]toluene, and [D_8]THF were distilled over CaH_2 and degassed before use. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with BRUKER AVANCEIII-400 and JEOL JNM-ESC400 spectrometers. Assignment of ^{1}H and ^{13}C NMR peaks for some of the complexes were facilitated by 2D ^{1}H-^{1}H COSY, 2D ^{1}H-^{13}C HMQC, and 2D ^{1}H-^{13}C HMBC spectra. GC-MS measurements were performed using a DB-1 capillary column (0.25 mm × 30 m) with a Shimadzu GCMS-QP2010Plus. All melting points were measured in sealed tubes under an argon atmosphere. UV/Vis spectra were recorded with an Agilent 8453. Elemental analyses were recorded with a PerkinElmer 2400 at the Faculty of Engineering Science, Osaka University.

Preparation of dinuclear tantalum complex 2

Complex **1** (3.01 g, 6.57 mmol) and $AlCl_3$ (876 mg, 6.57 mmol) were placed in an argon-filled Schlenk tube, and toluene (20 mL) was added by using a syringe. The reaction mixture was stirred at 80 °C for 30 min. The color of the solution changed from deep-orange to deep-purple. [$AlCl_3$(DME)] precipitated after hexane (40 mL) was added to the reaction mixture by using a syringe. The supernatant was transferred to another Schlenk tube, then all volatiles were removed under reduced pressure. The residue was recrystallized from a mixture of toluene and hexane (1:2 v/v) to give **2** (1.82 g, 2.46 mmol, 75%) as purple crystals; m.p. 101–103 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.91$ (t, $^3J = 7.7$ Hz, 6H; CβCH$_2$C*H*$_3$), 1.07 (t, $^3J = 7.3$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 2.81 (q, $^3J = 7.7$ Hz, 4H; CβC*H*$_2$CH$_3$), 3.45 ppm (q, $^3J = 7.3$ Hz, 4H; TaCαC*H*$_2$CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 13.6$ (CβCH$_2$CH$_3$), 17.3 (TaCαCH$_2$CH$_3$), 24.4 (CβCH$_2$CH$_3$), 36.5 (TaCαCH$_2$CH$_3$), 127.5 (CβCH$_2$CH$_3$), 224.0 (TaCαCH$_2$CH$_3$); UV/Vis (toluene): λ_{max} (ε, M^{-1} cm^{-1}) = 523 nm (4.0×10^2);

elemental analysis calcd (%) for $C_{12}H_{20}Cl_6Ta_2$: C 19.51, H 2.73; found: C 19.65, H 2.69.

Preparation of THF-coordinated dinuclear tantalum complex 3a

THF (1.0 mL, 12 mmol) was added by using a syringe to a solution of complex **2** (100 mg, 0.135 mmol) in toluene (2 mL) at RT. The reaction mixture was stirred for 5 min, then all volatiles were removed under reduced pressure to give **3a** (109 mg, 0.135 mmol, quantitative) as an orange powder; m.p. 115–116 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 303 K): $\delta = 1.16$ (t, $^3J = 7.4$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 1.29 (t, $^3J = 7.6$ Hz, 6H; CβCCH$_2$C*H*$_3$), 2.14–2.32 (m, 4H; β-THF), 2.7–3.9 (br, 4H; CβC*H*$_2$CH$_3$), 3.5–3.8 (br, 4H; TaCαC*H*$_2$CH$_3$), 4.62–4.88 ppm (m, 4H; β-THF); ^{13}C NMR (100 MHz, CD_2Cl_2, 303 K): $\delta =$ 17.4 (CβCH$_2$*C*H$_3$), 20.6 (TaCαCH$_2$*C*H$_3$), 24.4 (β-C of THF), 26.5 (CβCH$_2$CH$_3$) 40.7 (TaCαC*H*$_2$CH$_3$), 83.2 (α-C of THF), 159.0 (*C*βCH$_2$CH$_3$), 230.3 ppm (Ta*C*αCH$_2$CH$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 451 nm (9.5×10^2); elemental analysis calcd (%) for $C_{16}H_{28}Cl_6OTa_2$: C 23.70, H 3.48; found: C 24.02, H 3.60.

Preparation of pyridine-coordinated dinuclear tantalum complex 3b

Pyridine (21.4 mg, 0.270 mmol) was added by using a syringe to a solution of complex **2** (200 mg, 0.270 mmol) in toluene (3 mL) at RT. The reaction mixture was stirred for 5 min at RT, then cooled to −40 °C to form **3b** (172 mg, 0.210 mmol, 78%) as orange crystals; m.p. 120–121 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.68$ (t, $^3J = 6.8$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 0.93 (t, $^3J = 7.5$ Hz, 6H; CβCH$_2$C*H*$_3$), 2.42–2.64 (m, 2H; CβC*H*HCH$_3$), 3.21–3.45 (m, 2H; CβCH*H*CH$_3$), 3.57–3.85 (m, 4H; TaCαC*H*HCH$_3$, TaCαCH*H*CH$_3$), 6.29–6.40 (m, 2H; *m*-py), 6.65–6.73 (m, 1H; *p*-py), 9.0–9.2 (br, 2H; *o*-py); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 16.9$ (CβCH$_2$*C*H$_3$), 20.2 (TaCαCH$_2$*C*H$_3$), 24.1 (CβCH$_2$CH$_3$), 40.7 (TaCα*C*H$_2$CH$_3$), 124.6 (*p*-py), 140.5 (*m*-py), 152.1 (*o*-py), 158.8 (*C*βCH$_2$CH$_3$), 233.0 ppm (TaCαCH$_2$CH$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 319 (8.0×10^3), 462 nm (1.6×10^3); elemental analysis calcd (%) for $C_{17}H_{25}Cl_6NTa_2$: C 24.96, H 3.08, N 1.71; found: C 25.03, H 3.16, N 1.81.

Preparation of THT-coordinated dinuclear tantalum complex 3c

Complex **3c** was synthesized as described for **3a**. The reaction of **2** (300 mg, 0.406 mmol) with THT (0.10 mL, 1.1 mmol) in toluene (3 mL) gave **3c** (335 mg, 0.406 mmol, quantitative) as a red-orange powder; m.p. 106–108 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta =$ 0.92 (t, $^3J = 7.6$ Hz, 6H; CβCH$_2$C*H*$_3$), 1.05 (t, $^3J = 7.4$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 1.30–1.43 (m, 4H; β-THT), 2.74–2.94 (m, 8H; CβC*H*$_2$CH$_3$, α-THT), 3.58 ppm (q, $^3J = 7.4$ Hz, 4H; TaCαC*H*$_2$CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 16.3$ (CβCH$_2$*C*H$_3$), 18.8 (TaCαCH$_2$*C*H$_3$), 23.8 (CβCH$_2$CH$_3$), 30.3 (β-C of THT), 37.2 (α-C of THT), 39.6 (TaCα*C*H$_2$CH$_3$), 149.5 (*C*βCH$_2$CH$_3$), 226.8 ppm (TaCαCH$_2$CH$_3$); elemental analysis calcd (%) for $C_{16}H_{28}Cl_6STa_2$: C 23.24, H 3.41; found: C 23.28, H 3.32.

Preparation of a two-electron reduced μ-η^4:η^4-hexaethylbenzene and a μ-η^2:η^2-3-hexyne ligand-coordinated dinuclear tantalum complex 4 from complex 3a

A solution of 3-hexyne (141 μL, 1.23 mmol) in toluene (5 mL) was added by using a syringe to a solution of complex **3a** (100 mg, 0.123 mmol) in toluene (15 mL) at RT. The reaction mixture immediately became red. After stirring the reaction mixture for 1 h at RT, hexane (10 mL) was added to the mixture to form insoluble tantalum species and a small amount of poly(3-hexyne) as precipitates. The supernatant was transferred to another vial, then all volatiles were removed under reduced pressure. The residue was washed with hexane (3×5 mL), then the resulting precipitates were dried under reduced pressure to give **4** (20.0 mg, 0.0240 mmol, 20%) as a red powder; m.p. 217–218 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.39$ (t, $^3J = 7.5$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 0.72 (q, $^3J = 7.5$ Hz, 4H; TaCαC*H*$_2$CH$_3$), 1.07 (t, $^3J = 7.4$ Hz, 12H; CβCH$_2$C*H*$_3$), 1.53 (t, $^3J =$ 7.4 Hz, 6H; ≡CCH$_2$C*H*$_3$), 2.19 (dq, $^2J = 14.8$ Hz, $^3J = 7.4$ Hz, 4H; CβC*H*HCH$_3$), 2.77 (dq, $^2J = 14.8$ Hz, $^3J = 7.4$ Hz, 4H; CβCH*H*CH$_3$), 3.98 ppm (q, $^3J = 7.4$ Hz, 4H; ≡CC*H*$_2$CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 15.5$ (TaCαCH$_2$CH$_3$), 16.6 (≡CCH$_2$*C*H$_3$), 19.8 (CβCH$_2$CH$_3$), 23.8 (TaCαCH$_2$CH$_3$), 26.6 (CβCH$_2$CH$_3$), 38.7 (≡CCH$_2$CH$_3$), 104.5 (Ta*C*αCH$_2$CH$_3$), 108.7 (*C*βCH$_2$CH$_3$), 209.4 ppm (≡CCH$_2$CH$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 318 (8.3×10^3), 381 (3.0×10^3), 446 nm (6.3×10^3); elemental analysis calcd (%) for $C_{24}H_{40}Cl_4Ta_2$: C 34.63, H 4.84; found: C 34.79, H 4.81.

Preparation of low-valent tantalum complex 5 by Me$_4$-BTDP

Complex **2** (200 mg, 0.270 mmol) was placed in an argon-filled Schlenk tube, then toluene (3 mL) was added by using a syringe. A solution of Me$_4$-BTDP (76.5 mg, 0.270 mmol) in toluene (2 mL) was added to the Schlenk tube to form yellow precipitates. The reaction mixture was stirred at RT for 2 h. After all volatiles were removed under reduced pressure, the residue was washed with hexane (2×2 mL). The yellow solids were dried under reduced pressure to give **5** (180 mg, 0.270 mmol, quantitative) as a yellow powder; m.p. 303–304 °C (dec); ^{1}H NMR (400 MHz, [D$_8$]THF, 303 K): $\delta = 0.85$ (t, $^3J = 7.5$ Hz, 6H; TaCαCH$_2$C*H*$_3$), 1.61 (t, $^3J = 7.7$ Hz, 6H; CβCH$_2$C*H*$_3$), 3.10 (q, $^3J = 7.7$ Hz, 4H; CβC*H*$_2$CH$_3$), 3.16 ppm (q, $^3J =$ 7.5 Hz, 4H; TaCαC*H*$_2$CH$_3$); ^{13}C NMR (100 MHz, [D$_8$]THF, 303 K): $\delta =$ 12.8 (CβCH$_2$*C*H$_3$), 16.0 (TaCαCH$_2$*C*H$_3$), 27.8 (CβC*H*$_2$CH$_3$), 50.4 (TaCα*C*H$_2$CH$_3$), 106.0 (*C*βCH$_2$CH$_3$), 235.1 (TaCαCH$_2$CH$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 363 nm (1.6×10^3); elemental analysis calcd (%) for $C_{12}H_{20}Cl_4Ta_2$: C 21.58, H 3.02; found: C 21.77, H 3.40.

Preparation of complex 4 from 5

A solution of Me$_4$-BTDP (573 mg, 2.03 mmol) in toluene (15 mL) was added by using a syringe to a Schlenk tube containing a solution of **2** (1.50 g, 2.03 mmol) in toluene (40 mL) at RT. The reaction mixture was stirred at RT for 2 h to form yellow precipitates of **5**. After addition of 3-hexyne (463 μL, 4.06 mmol) to the yellow suspension by using a syringe, the reaction mixture immediately changed to a red suspension. All volatiles were removed under reduced pressure, then the residue was extracted with toluene (3× 30 mL). The solvent was evaporated to give a red powder, which was washed with hexane (20 mL) and dried under reduced pressure to give **4** (1.18 g, 1.42 mmol, 70%) as a red powder. The NMR spectral data in C_6D_6 was identical to that of complex **4** prepared from **3a** with an excess amount of 3-hexyne (as mentioned above).

Preparation of (Me$_3$SiC≡CSiMe$_3$)-coordinated dinuclear tantalum complex 6

A solution of Me$_4$-BTDP (382 mg, 1.35 mmol) in toluene (5 mL) was added to a solution of complex **2** (1.00 g, 1.35 mmol) and bis(trimethylsilyl)acetylene (460 mg, 2.70 mmol) in toluene (35 mL) at RT. The reaction mixture was stirred at 80 °C for 16 h. The purple supernatant was transferred to another Schlenk tube, then all volatiles were removed under reduced pressure. The purple residue was dried at 80 °C to give **6** (720 mg, 0.859 mmol, 64%) as

a purple powder; m.p. 105–107 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.49$ (s, 18H; $SiMe_3$), 1.03 (t, $^3J = 7.6$ Hz, 6H; CβCH$_2$CH_3), 1.17 (t, $^3J = 7.3$ Hz, 6H; TaCαCH$_2$CH_3), 2.3–2.6 (br, 4H; TaCαCH_2CH$_3$), 2.6–2.8 ppm (br, 4H; CβCH_2CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 2.7$ (≡CSiMe_3), 17.4 (TaCαCH$_2$CH$_3$), 17.5 (CβCH$_2$CH$_3$), 24.6 (CβCH$_2$CH$_3$), 36.1 (TaCαCH_2CH$_3$), 149.1 (CβCH$_2$CH$_3$), 249.2 (TaCαCH$_2$CH$_3$), 265.5 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 319 (6.5×10^3), 492 nm (1.7×10^3); elemental analysis calcd (%) for $C_{20}H_{38}Cl_4Si_2Ta_2$: C 28.65, H 4.57; found: C 28.45, H 4.26.

Preparation of dinuclear tantalum complex 7a from complex 6

2-Butyne (28.0 μL, 0.357 mmol) was added by using a microsyringe to a solution of complex **6** (100 mg, 0.119 mmol) in toluene (2 mL) at −40 °C, then the reaction mixture was stirred at RT for 16 h. After evaporation of all volatiles, the residue was washed with hexane (5 mL). Drying the precipitates gave **7a** (80.0 mg, 0.0896 mmol, 75%) as an orange powder; m.p. 264–265 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.44$ (t, $^3J = 7.4$ Hz, 6H; TaCαCH$_2$CH_3), 0.60 (s, 18H; $SiMe_3$), 0.91 (t, $^3J = 7.4$ Hz, 6H; CβCH$_2$CH_3), 1.05 (q, $^3J = 7.4$ Hz, 4H; TaCαCH_2CH$_3$), 2.03 ppm (s, 6H; CβMe); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 4.2$ ($SiMe_3$), 15.7 (TaCαCH$_2$CH$_3$), 18.7 (CβCH$_2$CH$_3$), 20.2 (CβMe), 25.3 (TaCαCH_2CH$_3$), 27.7 (CβCH_2CH$_3$), 107.9 (TaCαCH$_2$CH$_3$), 111.0 (CβMe), 116.1 (CβCH$_2$CH$_3$), 224.3 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 306 (3.8×10^3), 426 (2.5×10^3), 470 nm (2.1×10^3); elemental analysis calcd (%) for $C_{24}H_{44}Cl_4Si_2Ta_2$: C 32.30, H 4.97; found: C 32.60, H 4.95.

Preparation of dinuclear tantalum complex 7b from complex 6

Complex **7b** was synthesized as described for **7a**. The reaction of complex **6** (100 mg, 0.119 mmol) with 4-octyne (52.4 μL, 0.357 mmol) gave **7b** (90.0 mg, 0.098 mmol, 80%) as an orange powder; m.p. 263–264 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta =$ 0.45 (t, $^3J = 7.5$ Hz, 6H; TaCαCH$_2$CH_3), 0.62 (s, 18H; $SiMe_3$) 0.75 (t, $^3J = 7.3$ Hz, 6H; CβCH$_2$CH$_2$CH_3), 0.98 (t, $^3J = 7.4$ Hz, 6H; CβCH$_2$CH_3), 1.05 (q, $^3J = 7.5$ Hz, 4H; TaCαCH_2CH$_3$), 1.23–1.42 (m, 2H; CβCH$_2$CHHCH$_3$), 1.49–1.69 (m, 2H; CβCH$_2$CHHCH$_3$), 2.09–2.30 (m, 4H; CβCHHCH$_2$CH$_3$, CβCHHCH$_3$), 2.38–2.60 ppm (m, 4H; CβCHHCH$_3$, CβCHHCH$_2$CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 4.3$ ($SiMe_3$), 14.3 (CβCH$_2$CH$_2$CH$_3$), 15.3 (TaCαCH$_2$CH$_3$), 18.9 (CβCH$_2$CH$_3$), 25.7 (TaCαCH$_2$CH$_3$), 27.8 (CβCH$_2$CH$_3$), 28.1 (CβCH$_2$CH$_2$CH$_3$), 37.2 (CβCH$_2$CH$_2$CH$_3$), 107.5 (TaCαCH$_2$CH$_3$), 116.7 (CβCH$_2$CH$_2$CH$_3$), 117.8 (CβCH$_2$CH$_3$), 224.5 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$): 307 (3.7×10^3), 426 (2.2×10^3), 472 nm (1.9×10^3); elemental analysis calcd (%) for $C_{28}H_{52}Cl_4Si_2Ta_2$: C 35.45, H 5.53; found: C 35.10, H 5.00.

Isomerization of 7a to produce 7a′

Complex **7a** (65.0 mg, 0.0728 mmol) was placed in a Schlenk tube, then toluene (3 mL) was added. The solution was stirred at 80 °C for 1 h, then all volatiles were removed under reduced pressure to give **7a′** (65.0 mg, 0.0728 mmol, quantitative) as a red powder; mp 260–261 °C (dec.); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.47$ (t, $^3J =$ 7.5 Hz, 3H; TaCαCH$_2$CH_3), 0.59 (s, 9H; $SiMe_3$), 0.60 (s, 9H; $SiMe_3$), 0.66 (t, $^3J = 7.4$ Hz, 3H; CβCH$_2$CH_3), 0.84 (t, $^3J = 7.4$ Hz, 3H; CβCH$_2$CH_3), 0.88 (t, $^3J = 7.4$ Hz, 3H; CβCH$_2$CH_3), 0.94 (s, 3H; TaCαMe), 1.04–1.14 (m, 2H; TaCαCH_2CH$_3$), 1.92 (s, 3H; CβMe), 2.06–2.44 ppm (m, 6H; CβCH_2CH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta =$ 4.2 (2C, SiMe), 15.5 (TaCαCH$_2$CH$_3$), 15.6 (CβCH$_2$CH$_3$), 15.6 (CβCH$_2$CH$_3$), 17.8 (TaCα*Me*), 17.8 (Cβ*Me*), 17.9 (CβCH$_2$CH$_3$), 25.7 (TaCαCH$_2$CH$_3$), 26.0 (CβCH$_2$CH$_3$), 27.4 (CβCH$_2$CH$_3$), 27.8 (CβCH$_2$CH$_3$), 100.3 (TaCαMe), 105.8 (TaCαCH$_2$CH$_3$), 112.0 (CβMe), 115.4 (CβCH$_2$CH$_3$), 115.6 (CβCH$_2$CH$_3$), 116.7 (CβCH$_2$CH$_3$), 218.4 (≡CSiMe$_3$), 223.4 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 306 (4.0×10^3), 418 (2.7×10^3), 477 ppm (2.5×10^3); elemental analysis calcd (%) for $C_{24}H_{44}Cl_4Si_2Ta_2$: C 32.30, H 4.97; found: C 31.93; H 4.64.

Preparation of dinuclear tantalum complex 8a′ from complex 6

Complex **8a′** was synthesized as described for **7a**. The reaction of complex **6** (100 mg, 0.119 mmol) with 1-hexyne (14 μL, 0.12 mmol) gave **8a′** (97.0 mg, 0.105 mmol, 88%) as an orange powder; m.p. 216–217 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta = 0.49$ (t, $^3J =$ 7.5 Hz, 3H; TaCαCH$_2$CH_3), 0.60 (s, 9H; $SiMe_3$), 0.61 (s, 9H; $SiMe_3$), 0.76 (t, $^3J = 7.1$ Hz, 3H; CβCH$_2$CH_3), 0.80 (t, $^3J = 7.5$ Hz, 3H; CβCH$_2$CH_3), 0.91 (t, $^3J = 7.5$ Hz, 3H; CβCH$_2$CH_3), 0.94 (t, $^3J = 7.5$ Hz, 3H; CβCH$_2$CH_3), 1.08–1.29 (m, 6H; CβCH$_2$CH_2CH_2CH$_3$ and TaCαCH_2CH$_3$), 1.21 (s, 1H; TaCαH), 2.09–2.64 ppm (m, 8H; CβCHHCH$_2$CH$_2$CH$_3$ and CβCHHCH$_3$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 3.8$ (2C, $SiMe_3$), 13.9 (CβCH$_2$CH$_2$CH$_2$CH$_3$), 15.4 (TaCαCH$_2$CH$_3$), 16.3 (CβCH$_2$CH$_3$), 17.0 (CβCH$_2$CH$_3$), 17.1 (CβCH$_2$CH$_3$), 23.4 (TaCαCH$_2$CH$_3$), 25.5 (CβCH$_2$CH$_2$CH$_2$CH$_3$), 26.5 (CβCH$_2$CH$_3$), 26.6 (CβCH$_2$CH$_3$), 29.5 (CβCH$_2$CH$_3$), 35.3 (CβCH$_2$CH$_2$CH$_2$CH$_3$), 36.6 (CβCH$_2$CH$_2$CH$_2$CH$_3$), 89.0 (^1J(C,H) = 160 Hz; TaCαH), 106.6 (TaCαCH$_2$CH$_3$), 114.9 (CβCH$_2$CH$_3$), 115.2 (CβCH$_2$CH$_3$), 115.4 (CβCH$_2$CH$_3$), 115.6 (CβCH$_2$CH$_2$CH$_2$CH$_3$), 217.9 (≡CSiMe$_3$), 219.1 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$) = 303 (3.9×10^3), 408 (2.7×10^3), 486 nm (2.8×10^3); elemental analysis calcd (%) for $C_{24}H_{44}Cl_4Si_2Ta_2$: C 33.92, H 5.26; found: C 33.71, H 5.47.

Preparation of dinuclear tantalum complex 8b′ from complex 6

Complex **8b′** was synthesized as described for **7a**. The reaction of complex **6** (100 mg, 0.119 mmol) with *p*-tolylacetylene (13.2 μL, 0.120 mmol) gave **8b′** (102 mg, 0.107 mmol, 90%) as an orange powder; m.p. 227–228 °C (dec); ^{1}H NMR (400 MHz, C_6D_6, 303 K): $\delta =$ 0.54 (s, 9H; $SiMe_3$), 0.55 (t, $^3J = 7.4$ Hz, 3H; TaCαCH$_2$CH_3), 0.64 (s, 9H; $SiMe_3$), 0.72 (t, $^3J = 7.4$ Hz, 3H; CβCH$_2$CH_3), 0.93 (t, $^3J = 7.5$ Hz, 3H; CβCH$_2$CH_3), 0.96 (t, $^3J = 7.5$ Hz, 3H; CβCH$_2$CH_3), 1.28 (q, $^3J =$ 7.4 Hz, 2H; TaCαCH_2CH$_3$), 1.63 (s, 1H; CH), 2.05 (s, 3H; *Me*C$_6$H$_4$), 2.16–2.25 (m, 2H; CβCHHCH$_3$, CβCHHCH$_3$), 2.34–2.48 (m, 2H; CβCHHCH$_3$, CβCHHCH$_3$), 2.72 (dq, $^2J = 15.4$ Hz, $^3J = 7.6$ Hz, 1H; CβCHHCH$_3$), 3.20 (dq, $^2J = 14.9$ Hz, $^3J = 7.5$ Hz, 1H; CβCHHCH$_3$), 6.91 (d, $^3J = 8.1$ Hz, 2H; *m*-MeC$_6H_4$), 7.50 ppm (d, $^3J = 8.1$ Hz, 2H; *o*-MeC$_6H_4$); ^{13}C NMR (100 MHz, C_6D_6, 303 K): $\delta = 3.8$ (2C, $SiMe_3$), 15.2 (CβCH$_2$CH$_3$), 15.4 (TaCαCH$_2$CH$_3$), 15.5 (CβCH$_2$CH$_3$), 16.8 (CβCH$_2$CH$_3$), 21.0 (*Me*C$_6$H$_4$), 25.7 (TaCαCH$_2$CH$_3$), 26.0 (CβCH$_2$CH$_3$), 26.8 (CβCH$_2$CH$_3$), 29.1 (CβCH$_2$CH$_3$), 87.8 (^1J(C,H) = 158 Hz, TaCαH), 105.1 (TaCαCH$_2$CH$_3$), 111.4 (Cβtolyl), 114.8 (CβCH$_2$CH$_3$), 116.6 (CβCH$_2$CH$_3$), 116.9 (CβCH$_2$CH$_3$), 129.3 (*m*-C of tolyl), 130.9 (*o*-C of tolyl), 134.7 (*ipso*-C of tolyl), 139.5 (Me*C*), 220.1 (≡CSiMe$_3$), 220.1 ppm (≡CSiMe$_3$); UV/Vis (toluene): λ_{max} (ε, $M^{-1}cm^{-1}$): 306 (1.0×10^4), 414 (6.5×10^3), 483 nm (4.9×10^3); elemental analysis calcd (%) for $C_{24}H_{44}Cl_4Si_2Ta_2$: C 36.49, H 4.86; found: C 36.16, H 4.81.

Detection of 8a and 8b by low-temperature NMR measurements

In J-young NMR tubes, 1-hexyne (1.4 μL, 1 equiv., 0.012 mmol) or *p*-tolylacetylene (1.4 μL, 1 equiv., 0.012 mmol) was added by using a microsyringe at −78 °C to a solution of **6** in [D$_8$]toluene. These

NMR tubes were kept at −78 °C until NMR measurements. **8a**: ^{1}H NMR (400 MHz, [D$_8$]toluene, 263 K): $\delta = 0.45$ (t, $^3J = 7.5$ Hz, 3H; TaCαCH$_2$CH$_3$), 0.48 (s, 18H; SiMe$_3$), 0.51 (t, $^3J = 7.5$ Hz, 3H; TaCαCH$_2$CH$_3$), 0.71–1.70 (m, 17H; CβCH$_2$CH$_2$CH$_2$CH$_3$ and TaCαCH$_2$CH$_3$, CβCH$_2$CH$_3$), 2.08–2.80 (m, 6H; CβCHHCH$_2$CH$_2$CH$_3$ and CβCHHCH$_3$), 5.53 ppm (s, 1H; CβH); ^{13}C NMR (100 MHz, [D$_8$]toluene, 263 K): $\delta =$ 3.7 (SiMe$_3$), 4.0 (SiMe$_3$), 14.0, 14.1, 15.2, 17.7, 18.4, 23.2, 24.4, 25.3, 26.3, 28.1, 34.5, 35.3 (for 12 alkyl carbons), 102.2, 107.1, 107.3, 114.8, 115.1, 118.6 (for 6 arene ring carbons), 224.2 (≡CSiMe$_3$), 224.9 ppm (≡CSiMe$_3$). **8b**: ^{1}H NMR (400 MHz, [D$_8$]toluene, 213 K): $\delta = 0.09$ (t, $^3J = 7.3$ Hz, 3H; TaCαCH$_2$CH$_3$), 0.41 (t, $^3J = 7.3$ Hz, 3H; TaCαCH$_2$CH$_3$), 0.66 (s, 9H; SiMe$_3$), 0.70 (s, 9H; SiMe$_3$), 0.82 (t, $^3J =$ 7.3 Hz, 6H; CβCH$_2$CH$_3$), 0.91–1.38 (m, 4H; TaCαCH$_2$CH$_3$), 2.02 (s, 3H; Me), 2.13–2.30 (m, 4H; CβCH$_2$CH$_3$), 6.04 (s, 1H; CβH), 6.78 (d, $^3J =$ 8.0 Hz, 2H; *m*-MeC$_6$H$_4$), 7.65 ppm (d, $^3J = 8.0$ Hz, 2H; *o*-MeC$_6$H$_4$).

Catalytic alkyne trimerization catalyzed by tantalum complexes 1, 2 and 3a–c (Tables 2 and 3)

In J-young NMR tubes, tantalum complexes **1**, **2**, or **3a–c** (0.877 μmol, 0.5 mol% to alkynes), alkynes (0.175 mmol) and hexamethylbenzene or anthracene as an internal standard were dissolved in C_6D_6 (0.6 mL). The NMR tubes were allowed to stand at RT for 15 min, then ^{1}H NMR spectra of the samples were recorded to determine the product yield and the ratio of regioisomers.

Kinetic studies for isomeric reaction from 7a to 7a′

The rate constants for the isomerization of **7a** to **7a′** were determined by recording ^{1}H NMR spectra at several temperatures (Figure 5, top), and the activation parameters were estimated based on Eyring plots (Figure 5, bottom). Sample solutions for their ^{1}H NMR measurements ([**7a**]$_0 = 2.80$ mmol L^{-1}, [anthracene] = 33.6 mmol L^{-1} as an internal standard) were prepared by dissolving complex **7a** (16.6 mg, 0.0186 mmol) and anthracene (10.2 mg, 0.0572 mmol) in C_6D_6 in a measuring flask (5 mL), and then the solution was transferred into four J-young NMR tubes by using a syringe. The temperatures of the samples in a NMR probe were calibrated with ethylene glycol.[18] ^{1}H NMR spectra were then recorded every 31 seconds. The plots from 500 seconds to the half-life of **7a** were used to calculate the rate constants.

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