



Catalytic Performance of Tantalum- η^2 -Alkyne Complexes [TaCl₃(R¹C≡CR²)L₂] for Alkyne Cyclotrimerization

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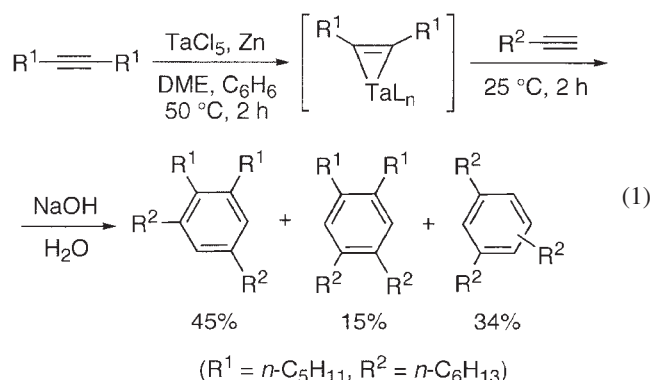
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Structurally characterized tantalum- η^2 -alkyne complexes [TaCl₃(η^2 -EtC≡CEt)L₂] (**1**, L₂ = 1,2-dimethoxyethane (DME); **2**, L = py) acted as catalysts for the cyclotrimerization of terminal alkynes. The catalytic reaction proceeded at 25 °C within few hours and the trisubstituted benzenes were obtained without the formation of linear oligomers. A new tantalum complex having a terminal alkyne ligand, [TaCl₃(η^2 -Me₃SiC≡CH)(dme)] (**3**), was prepared, and its catalytic performance was also investigated.

The transition metal-catalyzed cyclotrimerization of alkynes is one of the most attractive methods and atom economical processes for the construction of aromatic rings.^{1–8} Recent research in this field has been focused mainly on the regioselective formation of substituted aromatic compounds⁹ and the development of new early transition metal catalysts^{10–14} besides improvements of conventional late transition metal catalysts.^{15–17} An η^2 -alkyne complex of an early transition metal is of potential utility as a cyclotrimerization catalyst, because the cyclotrimerization proceeds via the insertion of an alkyne into a metal-alkyne bond of the alkyne complex. However, the isolated η^2 -alkyne complexes of group 5 metals, except for Wigley's [(DIPP)₃Ta(η^2 -RC≡CR') (DIPP = 2,6-diisopropylphenoxide),^{18,19} are known to be inert toward the insertion of alkynes, which is the first step of cyclotrimerization.^{20,21} In fact, catalytically active group 5 η^2 -alkyne complexes have been prepared in situ in many previous studies.^{10,22–29} In 1995, we reported that the stoichiometric cyclotrimerization proceeded when the treatment of terminal alkynes with low-valent tantalum complexes generated in situ (Eq. 1).³⁰ Recently, we isolated and determined the structures of several tantalum- η^2 -internal alkyne complexes with the general formula, [TaCl₃(η^2 -RC≡CR')(dme)], which were postulated as the intermediates of cyclotrimerization.³¹ In this paper we report on the catalytic behavior of [TaCl₃(η^2 -EtC≡CEt)(dme)] (**1**) and [TaCl₃(η^2 -EtC≡CEt)(py)₂] (**2**) as single-component terminal alkyne cyclotrimerization catalysts (Scheme 1). In addition, a new tantalum complex having a terminal alkyne ligand, [TaCl₃(η^2 -Me₃SiC≡CH)(dme)] (**3**), has been synthesized and

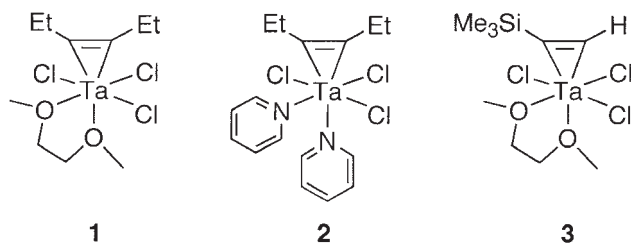
characterized; its catalytic behavior toward trimethylsilylacetylene is also presented.



Results and Discussion

Tantalum-3-hexyne Complexes 1 and 2 Catalyzed Cyclotrimerization. The catalytic behavior of the structurally characterized 3-hexyne complex **1**³¹ toward the cyclotrimerization of 1-hexyne was investigated. The reaction of 1-hexyne catalyzed by 1 mol% of **1** proceeded in toluene at 25 °C for 18 h to give 1,2,4-tributylbenzene and 1,3,5-tributylbenzene in almost quantitative yield with 72:28 isomeric ratio (Table 1, run 1). No linear oligomer was formed, and a trace amount of dibutyl-diethylbenzene was detected, which was derived from 1-hexyne and coordinated 3-hexyne. The [2 + 2] cycloaddition is known to be exothermic.^{4,22} Actually, upon the addition of 1-hexyne to a solution of **1** in toluene, the solvent toluene began to boil. The reaction pathway of the cyclotrimerization can be explained by a 'common mechanism'⁵ involving the formation of tantalacyclopentadiene and tantalum- η^2 -terminal alkyne complexes. Therefore, the regioisomeric ratio (A:B = 72:28) of the cyclotrimerization of 1-hexyne is statistical, which are explained by a random insertion of 1-hexyne into the tantalum- η^2 -hexyne bond of **1** due to the less bulky ligand.

At low catalyst concentrations (S/C = 1000), the reaction

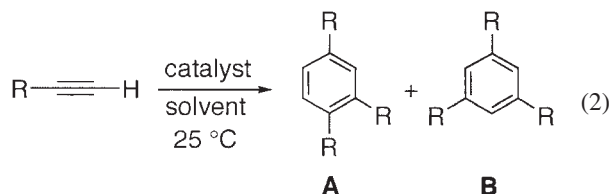


Scheme 1.

Table 1. Tantalum- η^2 -Alkyne Complex Catalyzed Cyclotrimerization of Terminal Alkynes (RC≡CH)

Run	Cat.	R	S/C	Solvent	Time/h	Yield/% A + B	Isomer ratio A/B
1	1	<i>n</i> -Bu	100	toluene	18	99	72/28
2	1	<i>n</i> -Bu	1000	toluene	23	25	74/26
3	1	<i>n</i> -Bu	100	hexane	1.5	99	76/24
4	1	<i>n</i> -Bu	100	CH ₂ Cl ₂	1.5	88	68/32
5	1	<i>n</i> -Bu	100	CH ₃ CN	1.5	trace	—
6	1	<i>n</i> -Bu	100	DME	1.5	0	—
7	1	<i>n</i> -Bu	100	THF	1.5	0	—
8	1	Ph	100	toluene	20	93	58/42
9	1	Me ₃ Si	100	hexane	20	99	52/48
10	1	HOCH ₂	100	toluene	7	0	—
11	2	<i>n</i> -Bu	100	toluene	1.5	56	44/56
12	3	Me ₃ Si	100	hexane	20	99	52/48

stopped at 25% conversion is probably due to the deactivation of the catalyst caused by the contamination of a trace amount of oxygen (run 2). As the solvent, hexane gave the best results, and the reaction was completed within 1.5 h (>99% conversion), whereas dichloromethane led to incomplete conversion (run 4). The cyclotrimerization was suppressed by the donor solvents, such as acetonitrile, DME, and THF (runs 5–7). In the case of acetonitrile, pyridine derivatives derived from acetonitrile and 1-hexyne were not detected. Phenylacetylene and trimethylsilylacetylene were also trimerized with **1** in almost quantitative yields (runs 8 and 9). Complex **1** did not catalyze the cyclotrimerization of 2-propargyl alcohol, due to the decomposition of the catalyst by the hydroxy group (run 10). An internal alkyne, such as 1-phenylpropyne and 3-hexyne, did not react with **1** at all. The catalytic reaction using bis(pyridine) catalyst **2** was sluggish (run 11), which is presumably due to a restraint of coordination of 1-hexyne to the tantalum center by the strongly coordinated pyridine ligands. Although the isomer ratio is low, 1,3,5-tributylbenzene was obtained as a major isomer.



Synthesis and Characterization of Tantalum- η^2 -Terminal Alkyne Complex **3 and Its Catalytic Performance.** Although an tantalum- η^2 -terminal alkyne intermediate would certainly be formed in the catalytic cycle, isolated η^2 -terminal alkyne complexes are still unknown. We chose trimethylsilylacetylene (Me₃SiC≡CH) as a sterically bulky terminal alkyne, and tried to isolate the tantalum- η^2 -terminal alkyne complex. The treatment of the low-valent tantalum with Me₃SiC≡CH gave **3** in 22% isolated yield as a brown crystalline solid. Complex **3** is the first example of a tantalum complex having an η^2 -terminal alkyne ligand. The thermally stable **3** could be stored at room temperature under argon for one year without decomposition. Complex **3** is also stable in organic solvents in the absence of oxygen and water. The η^2 -coordination of the alkyne and coordination environment around the tantalum was confirmed by NMR and IR spectroscopies. The terminal hydrogen

signals of Me₃SiC≡CH appeared at a remarkable lower field of δ 15.15 compared to that of the reported Pedersen's niobium analogue.²⁶ In the ¹³C{¹H} NMR spectral data, the two signals of alkyne carbon were observed at δ 239.1 and 255.3, which are comparable to those reported for tantalum- η^2 -alkyne complexes.^{21,32,33} Moreover, the IR absorption band at 1556 cm⁻¹ supports the η^2 -coordination mode of the alkyne fragment. Thus, the alkyne ligand donates four electrons to the tantalum center, and the canonical structure of the tantalum-alkyne unit can be best described as a tantalacyclopentadiene.^{34,35} The inequivalent methyl resonances of the coordinated DME ligand (δ 3.32 and 3.68 in ¹H NMR and δ 62.6 and 68.2 in ¹³C{¹H} NMR) indicate that one of the oxygen occupies the *trans* position to the alkyne ligand.³⁶ We conclude that the coordination environment around the tantalum of **1c** is essentially the same as those observed for Pedersen's [NbX₃(η^2 -alkyne)(dme)] (X = Cl, Br)²⁶ and our crystallographically characterized [TaCl₃(η^2 -alkyne)(dme)].³¹ The observation of the methylene protons of the DME as a singlet peak (δ 3.10) accords with that reported in the case of [NbBr₃(η^2 -EtC≡CEt)(dme)].²⁶

The reaction of **3** with 100 equiv of Me₃SiC≡CH proceeded smoothly to give tris(trimethylsilyl)benzenes in quantitative yield without the formation of any organic by-products, such as linear oligomer (run 12). Thus, the isolated η^2 -terminal alkyne complex **3** also catalyzed the cyclotrimerization, and coordinated Me₃SiC≡CH was completely incorporated into the cyclotrimers. The same isomer ratio as in the case of **1** (run 9) indicates that the cyclotrimerization by **3** probably proceeded via the same intermediate in **1** catalyzed cyclotrimerization.

Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under argon. 1,2-Dimethoxyethane (DME), THF, and toluene were purchased from Wako Pure Chemical Industries, Ltd. and stored on 4A molecular sieves under argon. Tantalum(V) chloride was purchased from Nacalai Tesque, Inc. tantalum- η^2 -alkyne complexes [TaCl₃(η^2 -EtC≡CEt)(dme)] (**1**) and [TaCl₃(η^2 -EtC≡CEt)(py)₂] (**2**) were prepared according to our previously described procedure.³¹ ¹H and ¹³C{¹H} NMR spectra were measured on a JEOL JNM-LA400 spectrometer. All ¹H NMR chemical shifts were reported in ppm relative to the protio impurity resonance as follows: CDCl₃, singlet at 7.26 ppm; C₆D₆, singlet at 7.20 ppm. IR spectra

were recorded using Nicolet PROTÉGÉ 460-T. The melting point was measured in a sealed tube on a Yanaco MP-S3 apparatus and was uncorrected.

Preparation of $[\text{TaCl}_5(\text{Me}_3\text{SiC}\equiv\text{CH})(\text{dme})]$ (3**).** Toluene (12 mL) was added to TaCl_5 (594 mg, 1.66 mmol) in a 80 mL Schlenk tube, and then DME (12 mL) was slowly added to the resulting yellow suspension. Zn powder (163 mg, 2.49 mmol) was added to the mixture in one portion at room temperature. After stirring the mixture at room temperature for 60 min, low-valent tantalum was prepared in almost quantitative yield. Trimethylsilylacetylene (235 μL , 1.66 mmol) was added to the suspension and stirred at 25 °C for 2 h. All volatiles were removed in vacuo, and the resulting pale brown powder was extracted with toluene (15 mL). Hexane (20 mL) was added as a layer to the solution, and placed in a -20 °C freezer. Upon standing overnight, brown crystals were deposited. Removal of the supernatant by a syringe afforded 174 mg (0.37 mmol) of **3** in 22% yield. Mp 105 °C (dec). IR (nujol/CsI) 1556 ($\nu_{\text{C}\equiv\text{C}}$), 309 ($\nu_{\text{Ta-Cl}}$) cm^{-1} . ^1H NMR (C_6D_6) δ 0.61 (s, 9H, $(\text{CH}_3)_3\text{Si-}$), 3.10 (s, 4H, $-\text{OCH}_2\text{CH}_2\text{O-}$), 3.32 (s, 3H, $-\text{OCH}_3$), 3.68 (s, 3H, $-\text{OCH}_3$), 15.15 (s, 1H, $\text{HC}\equiv$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 0.3 ($(\text{CH}_3)_3\text{Si-}$), 62.6 ($-\text{OCH}_3$), 68.2 ($-\text{OCH}_3$), 70.9 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 75.4 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 239.1 ($\equiv\text{CSi}$), 255.3 ($\text{HC}\equiv$).

Catalytic Cyclotrimerization of Terminal Alkynes. A typical procedure is described for the trimerization of 1-hexyne catalyzed by **1**. To a yellow solution of **1** (34.8 mg, 7.57 μmol) in toluene (5 mL) was added 1-hexyne (0.87 mL, 7.57 mmol), which was stirred at 25 °C for 18 h. After the reaction, the reaction mixture expose to the air and a small amount of silica gel was added. The mixture was passed through a short column on silica gel (hexane as an eluent) to remove any inorganic products, and all volatiles were removed in vacuo to give tributylbenzenes (620 mg, 2.52 mmol). The isomer ratio of the products was analyzed by gas chromatography (Quadrex 007 OV-17 (50 m $\times$ 0.32 mm)) and ^1H NMR spectroscopy.

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