Dinuclear Niobium(III) Complexes [{$NbCl_2$(L)}$_2$(μ-Cl)$_2$(μ-L)] (L = tetrahydrothiophene, dimethyl sulfide): Preparation, Molecular Structures, and the Catalytic Activity for the Regioselective Cyclotrimerization of Alkynes

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Received February 3, 2006

Dinuclear niobium complexes [{$NbCl_2L$}$_2$(μ-Cl)$_2$(μ-L)] (L = tetrahydrothiophene C_4H_8S, THT (**1a**)) have been prepared by the reaction of diniobium(V) decachloride (Nb_2Cl_{10}) with magnesium in THT. The structure of **1a** was determined by X-ray crystallography to have a Nb−Nb bond, which is consistent with that of **1b** (L = dimethyl sulfide, Me_2S). The reaction of **1a**, as well as **1b**, with alkyne ($R_1C\equiv CR_2$) at room temperature gave a head-to-tail cycloadded alkyne trimer, 1,3,5-(R_1)$_3$-2,4,6-(R_2)$_3$-benzene (R_1 = H, R_2 = Ph (**2**); R_1 = *p*-tolyl, R_2 = H (**3**); $R_1 = R_2 = CH_2Cl$ (**4**); $R_1 = R_2$ = COOEt (**5**); R_1 = *n*-Pr, R_2 = Me (**6**); R_1 = *n*-Bu, R_2 = H (**7**); $R_1 = Me_3Si$, R_2 = H (**8**), $R_1 = R_2$ = Et (**9**), $R_1 = R_2$ = *n*-Pr (**10**)), regioselectively in high yields. The cyclotrimerization is found to be catalyzed by complexes **1a** and **1b**, since only 1/600 equiv of the complex to the alkynes can lead to the corresponding product in high yields. The reactions of **1a** with 6 equiv of 3-hexyne and 4-octyne gave a mononuclear byproduct, $NbCl_3$(η^2-RC=CR−RC=CR) (R = Et (**11**), Pr (**12**)), besides **9** and **10**, respectively. The reactions of **11** or **12** with an excess of original alkyne, however, resulted exclusively in the formation of the corresponding benzene derivative, in equimolar amount to 1,2,3,4-(R)$_4$-5,6-(R′)$_2$-benzene (R = R′ = Et (**9**), R = R′ = Pr (**10**), R = Et, R′ = Pr (**13**), R = *n*-Pr, R′ = Et (**14**)). This observation suggests that the mononuclear species does not behave as a catalyst, and the regioselectivity may be due to a dinuclear structure of the niobium complexes.

1. Introduction

The chemistry of the lower oxidation states of niobium and tantalum in discrete complexes remains relatively unexplored. The first structurally characterized niobium(III) complex with halides is a class of metal−metal bonded dinuclear salts $M_3[Nb_2X_9]$ (M = Rb, Cs; X = Cl, Br, I) reported in 1970.[1] The observed Nb−Nb distances (2.60−2.86 Å)[2] and the diamagnetic behavior suggest that there is a Nb−Nb bond with a formal bond order 2. Subsequently, the neutral dinuclear complexes with sulfur donors [$Nb_2Cl_6L_3$] (L = tetrahydrothiophene THT, dimethyl sulfide Me_2S) were characterized by spectroscopic methods. These complexes have a triply bridged bioctahedral structure with one THT as a bridging ligand.[3] The diamagnetic (not antiferromagnetic) character despite the oxidation state +3 for both Nb centers suggests the strong Nb−Nb interaction. We have already carried out X-ray determinations of the structure of [$Nb_2Cl_6L_3$].[4]

The tantalum(III) analogue [$Ta_2X_6L_3$] (X = Cl, Br; L = Me_2S, THT) was also investigated by single-crystal X-ray techniques as well as spectroscopic methods,[5] to determine that the structure was identical to that of the corresponding Nb complex. Furthermore, the reaction of the Ta complex [{$TaCl_2$(THT)}$_2$(μ-Cl)$_2$(μ-THT)] with an alkyne $MeC\equiv C^tBu$ was found to form [$TaCl_2$(THT)(η^2-$MeC\equiv C^tBu$)(μ-Cl)]$_2$, and the structure was determined by X-ray crystallography.[6]

On the other hand, it was known that many metals and their complexes catalyze the [2+2+2] cyclotrimerization of alkynes to give benzene derivatives.[7−23] Among these catalysts, there

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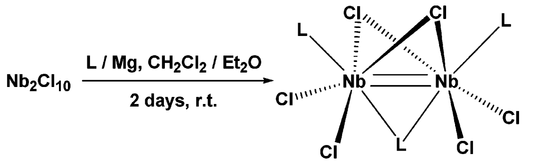
are mononuclear Nb and Ta complexes, $NbCl_3(DME)$[17] and $TaCl_3(DME)$[18] (DME = 1,2-dimethoxyethane). Products of these catalytic reactions have always been a mixture of 1,3,5- and 1,2,4-cyclotrimers, which is formed through both head-to-tail and head-to-head additions, respectively, and the yields generally do not depend on the substituents on the alkynes. In the past 50 years, the regio- and chemoselectivity for the cyclotrimerization of alkynes are the major challenge of synthetic chemists.[20] In this paper, we will report a novel regioselective and highly chemoselective process for preparing benzene derivatives via $Nb_2Cl_6(THT)_3$- or $Nb_2Cl_6(Me_2S)_3$-catalyzed cyclotrimerization of alkynes.

2. Results and Discussion

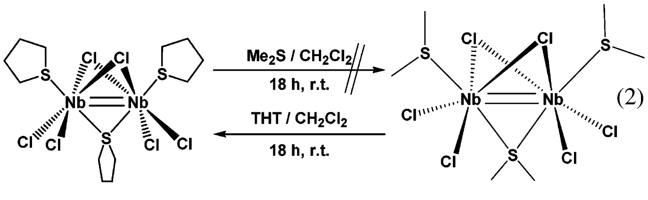
Syntheses of the Complexes. Although dinuclear niobium(III) complexes $[\{NbCl_2(L)\}_2(\mu\text{-}Cl)_2(\mu\text{-}L)]$ (**1a**, L = THT; **1b**, L = Me_2S) are known,[3] we developed a new route for the preparation. The reaction of diniobium(V) decachloride (Nb_2Cl_{10}) with magnesium and L in a mixture of dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) for 2 days provides **1a** and **1b**, in 86% and 88% yields, respectively, as shown in eq 1. The application of Mg as a reducing agent may give the targeted products in high yields. Single crystals were also successfully obtained probably because of the high purity. The molecular structures of **1a** (vide infra) and **1b**[4] as single crystals were determined by X-ray crystallography. The ^1H, ^{13}C, and ^{93}Nb NMR spectra in $CDCl_3$ suggest that the molecular structures in the solid state remain unchanged in solution. The diamagnetism of these complexes is rationalized by the formation of a Nb−Nb double bond, although the oxidation number of Nb is +3 with d^2 electron configuration.



(1)

1a (L = THT)
1b (L = Me$_2$S)

Complex **1a** did not react with Me_2S, while the reaction of **1b** with THT gave **1a**, as illustrated in eq 2. These results indicate that **1a** has a higher stability than **1b** and higher activation energy for the ligand substitution. This difference may reflect the strength of the coordination bond of Nb to the sulfur donor: greater electron-donating ability of THT than Me_2S.



(2)

1a **1b**

X-ray Crystallographic Study. Crystal Structure of 1a. The molecule contains a triply bridged dinuclear core "$\{Nb_2(\mu\text{-}Cl)_2(\mu\text{-}THT)\}$" with the THT rings in the same orientation with respect to the remainder of the molecule, as shown in Figure 1.

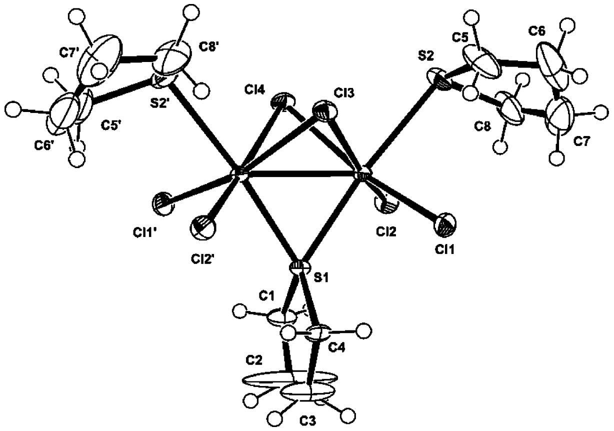


Figure 1. ORTEP drawing of **1a** with the numbering scheme.

Table 1. Crystal Data and Structure Refinement for 1a

empirical formula	$C_{12}H_{24}Cl_6Nb_2S_3$
fw	663.01
temperature	173(2) K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	*Pnma*
unit cell dimens	$a = 11.749(2)$ Å, $\alpha = 90°$
	$b = 20.215(4)$ Å, $\beta = 90°$
	$c = 9.792(2)$ Å, $\gamma = 90°$
volume	2325.7(8) $Å^3$
Z	4
density (calcd)	1.888 Mg/m^3
absorption coeff	1.940 mm^{-1}
$F(000)$	1312
cryst size	$0.15 \times 0.12 \times 0.10$ mm^3
θ range for data collection	2.01−27.93°
index ranges	$-15 \leq h \leq 15, -26 \leq k \leq 23, -12 \leq l \leq 9$
no. of reflns collected	15 905
no. of indep reflns	2851 [R(int) = 0.0974]
completeness to $\theta = 27.93°$	99.4%
absorp corr	semiempirical from equivalents
max. and min. transmn	0.8297 and 0.7596
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2851/0/115
goodness-of-fit on F^2	1.013
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0456$, $wR_2 = 0.0906$
R indices (all data)	$R_1 = 0.0626$, $wR_2 = 0.0964$
largest diff peak and hole	1.034 and −0.958 e $Å^{-3}$

The molecular structure is very similar to that of **1b** already reported elswhere.[4] There are few significant differences in the structural parameters of the molecule, as reflected in the bond distances and angles listed in Tables 1 and 2.

The shared trigonal face consists of one sulfur of THT and two chlorides in a pseudo-octahedral environment around each Nb, which is completed by two terminal chlorides and one terminal THT. Formation of the metal−metal bonding is obvious from the Nb−Nb distance, 2.6956(9) Å, which coincides within the range of atomic distances of $Nb^{III}-Nb^{III}$ double bonds, 2.60−2.86 Å. A further indication of the strong metal−metal attraction is the displacement of each Nb, ca. 0.20 Å, toward one another, away from the center of the idealized octahedral coordination sphere.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a

	Bond Lengths		
Nb(1)−Nb(1)#	2.6956(9)	S(1)−Nb(1)#	2.4370(11)
Cl(1)−Nb(1)	2.3879(11)	Nb(1)−S(2)	2.6573(12)
Cl(2)−Nb(1)	2.3853(11)	Nb(1)−S(1)	2.4370(11)
Cl(3)−Nb(1)#	2.5058(12)	Cl(3)−Nb(1)	2.5059(12)
Cl(4)−Nb(1)	2.5136(12)	Cl(4)−Nb(1)#	2.5136(12)
	Bond Angles		
Cl(1)−Nb(1)−Cl(2)	101.82(4)	Cl(1)−Nb(1)−Cl(3)	91.64(4)
Cl(1)−Nb(1)−Cl(4)	166.32(5)	Cl(1)−Nb(1)−S(1)	87.30(4)
Cl(2)−Nb(1)−S(1)	90.11(4)	Cl(1)−Nb(1)−S(2)	87.41(4)
Cl(2)−Nb(1)−Cl(3)	163.59(5)	Cl(2)−Nb(1)−Cl(4)	89.16(4)
Cl(2)−Nb(1)−S(2)	88.17(4)	Cl(3)−Nb(1)−Cl(4)	76.29(5)
Cl(3)−Nb(1)−S(1)	99.96(4)	Cl(3)−Nb(1)−S(2)	83.06(4)
Cl(4)−Nb(1)−S(2)	84.77(4)	Cl(4)−Nb(1)−S(1)	100.97(4)
Nb(1)−Cl(3)−Nb(1)#	65.08(4)	S(1)−Nb(1)−S(2)	173.98(4)
Nb(1)−Cl(4)−Nb(1)#	64.85(4)	Nb(1)−S(1)−Nb(2)	67.15(4)
C(1)−S(1)−C(4)	94.8(3)	C(8)−S(2)−C(5)	92.8(3)

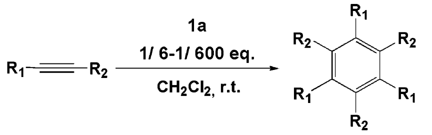
The Nb−S bond lengths for the bridging and terminal THT's are 2.44 and 2.66 Å, respectively, while the Nb−Cl lengths for the bridging and terminal chlorides are 2.51 and 2.39 Å, respectively. The Nb−(μ-S)−Nb and average Nb−(μ-Cl)−Nb angles are 67.15(4)° and 64.97(4)°, respectively. These features suggest stronger bonds to the bridging THT than those of terminal ones in the THT−Nb−THT axis, while the terminal Nb−Cl bonds are stronger than those of bridging Nb−Cl in the Cl−Nb−Cl axis.

These differences in coordination bond lengths and bridging angles may come from the nature of the bond. The normal coordination radius of S^{2-} (1.84 Å) is very similar to that of Cl^{-} (1.81 Å),[24] and electronic factors may be responsible for the difference. The bridging sulfur atom (μ-S) donates p electrons into a vacant d-orbital of each Nb center to form a σ-bond, and the low-lying vacant d-orbital of μ-S receives d electrons from one of the Nb−Nb bonds, forming a back-donating π-bond. On the other hand, the sulfur atom of the terminal sulfide (η-S) binds only through a donating σ-bond to each Nb metal center, since Nb has no available d electrons because of the formation of the Nb−Nb bond. Sulfur is not a strong electron-donating atom, and the μ-S interacts much stronger than the η-S does.

Chloride is different from sulfur in the lack of the vacant d-orbitals. Therefore, the bridging Cl^{-} cannot receive d electrons from the Nb centers as well as the Nb−Nb bond. On the contrary, the repulsion of Nb−Nb bonding electrons and chloride may elongate the Nb−(μ-Cl) bond and the Nb−Cl−Nb angle becomes smaller. This may be the reason Nb−(μ-Cl) is longer than Nb−(η-Cl).

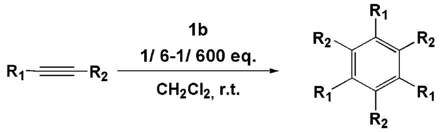
Cyclotrimerization of Monoalkynes. General Features. Reactions of **1a** and **1b** with an excess of alkynes under argon atmosphere at room temperature gave benzene derivatives. This cyclotrimerization of alkyne is found to be catalyzed by the present complexes, since only 1/600 equiv of the complex to the alkynes can lead to the product in high yields. The most remarkable feature is that the reaction gave only a corresponding head-to-tail cyclotrimerized product, i.e., 1,3,5-substituted benzene, from each alkyne. Scheme 1 shows benzene derivatives (R_1 = H, R_2 = Ph (**2**); R_1 = *p*-tolyl, R_2 = H (**3**); R_1 = R_2 = CH_2Cl (**4**); R_1 = R_2 = COOEt (**5**); R_1 = *n*-Pr, R_2 = Me (**6**); R_1 = *n*-Bu, R_2 = H (**7**); R_1 = Me_3Si, R_2 = H (**8**); R_1 = R_2 = Et (**9**), R_1 = R_2 = *n*-Pr (**10**))[25–33] given by the reaction of 6, 200, or 600 equiv of alkynes with **1a**. Scheme 2 shows benzene derivatives (**2**, **3**, **5**, **7**, **9**, and **10**)[25,26,28,30,32,33] of 6, 200, or 600 equiv of alkynes with **1b**. Compounds **2**−**10** were identified by ^{1}H NMR, FAB-MS, and melting point measurements.

Scheme 1. Cyclotrimerization of Alkynes Catalyzed by [{NbCl$_2$(THT)}$_2$(μ-Cl)$_2$(μ-THT)] (1a)



2 (R_1 = H, R_2 = Ph)
3 (R_1 = *p*-tolyl, R_2 = H)
4 (R_1 = R_2 = CH_2Cl)
5 (R_1 = R_2 = COOEt)
6 (R_1 = *n*-Pr, R_2 = Me)
7 (R_1 = *n*-Bu, R_2 = H)
8 (R_1 = $SiMe_3$, R_2 = H)
9 (R_1 = R_2 = Et)
10 (R_1 = R_2 = *n*-Pr)

Scheme 2. Cyclotrimerization of Alkynes Catalyzed by [{NbCl$_2$(Me$_2$S)}$_2$(μ-Cl)$_2$(μ-Me$_2$S)] (1b)



2 (R_1 = H, R_2 = Ph)
3 (R_1 = *p*-tolyl, R_2 = H)
5 (R_1 = R_2 = COOEt)
7 (R_1 = *n*-Bu, R_2 = H)
10 (R_1 = R_2 = *n*-Pr)

Tables 3 and 4 summarize the results of **1a**- and **1b**-catalyzed cyclotrimerization of alkynes to give benzene derivatives under various conditions, respectively. When the precursor is an alkyne with electron-withdrawing substituents, the reaction provides the head-to-tail cyclotrimer almost exclusively in a high yield in 0.17−4 and 4−18 h for **1a** and **1b**, respectively, even if only 1/600 equiv of the complex was applied to the alkynes. On the other hand, when the initial alkyne has electron-donating groups, the required duration is longer (4−18 h) and the yield is lower when the amount ratio of the complex to the reactant is low. Therefore, for both catalysts the cyclotrimerization rates are higher for alkynes with electron-withdrawing groups than those with electron-donating ones.

Elucidation of the Mechanism. Isolation of a Mononuclear Species. Scheme 3 shows reactions of **1a** with alkynes in CH_2Cl_2. The reaction of **1a** with a large excess of 3-hexyne and 4-octyne gave only 1,2,3,4,5,6-hexaethylbenzene (**9**)[32] and 1,2,3,4,5,6-hexapropylbenzene (**10**), respectively.[33] When 6 equiv of 3-hexyne and 4-octyne were mixed with **1a**, mononuclear complexes with 1,4-η^2-1,2,3,4-tetraalkylbutadiene [$NbCl_3$(η^2-RC=CR−RC=CR)] (R = Et (**11**), R = *n*-Pr (**12**)) were formed as byproducts of **9** and **10**, respectively. These mononuclear complexes were identified by ^{1}H NMR and FAB-MS. Reaction of isolated **11** and **12** with 1 equiv of 3-hexyne and 4-octyne, respectively, gave only **9**[32] and **10**,[33] respectively, and the cross reactions of **11** with 4-octyne and **12** with 3-hexyne provided **13**[23] and **14**, respectively, as shown in Scheme 3.

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Table 3. Cyclotrimerization of Alkynes to Benzene Derivatives Catalyzed by Complex 1a^{a} under Various Conditions in CH_2Cl_2 at Room Temperature.

entry	R_1	R_2	product	yield (%)
1^{b,g}	H	Ph	**2**	98
2^{c,f}	H	Ph	**2**	91
3^{d,f}	H	Ph	**2**	22
4^{b,g}	*p*-tolyl	H	**3**	97
5^{c,f}	*p*-tolyl	H	**3**	11
6^{d,f}	*p*-tolyl	H	**3**	3
7^{b,g}	CH_2Cl	CH_2Cl	**4**	97
8^{c,e}	CH_2Cl	CH_2Cl	**4**	95
9^{d,e}	CH_2Cl	CH_2Cl	**4**	18
10^{b,g}	COOEt	COOEt	**5**	92
11^{c,e}	COOEt	COOEt	**5**	90
12^{d,e}	COOEt	COOEt	**5**	20
13^{b,g}	*n*-Pr	Me	**6**	78
14^{c,f}	*n*-Pr	Me	**6**	16
15^{d,f}	*n*-Pr	Me	**6**	5
16^{b,g}	*n*-Bu	H	**7**	83
17^{c,f}	*n*-Bu	H	**7**	30
18^{d,f}	*n*-Bu	H	**7**	8
19^{b,g}	$SiMe_3$	H	**8**	75
20^{c,f}	$SiMe_3$	H	**8**	16
21^{d,f}	$SiMe_3$	H	**8**	3
22^{b,h}	Et	Et	**9**	60
23^{c,f}	Et	Et	**9**	10
24^{d,f}	Et	Et	**9**	2
25^{b,h}	*n*-Pr	*n*-Pr	**10**	40
26^{c,f}	*n*-Pr	*n*-Pr	**10**	8
27^{d,f}	*n*-Pr	*n*-Pr	**10**	2

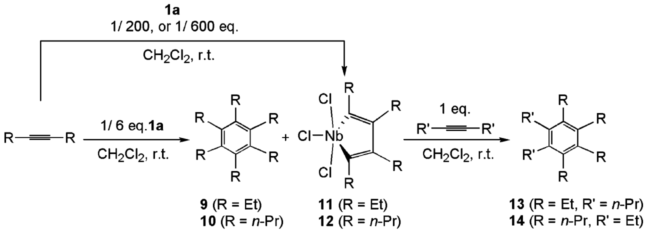
^{a} [complex **1a**] = 50 mg (0.075 mmol) in 20 mL of CH_2Cl_2. ^{b} [alkyne]/[complex **1a**] = 6. ^{c} [alkyne]/[complex **1a**] = 200. ^{d} [alkyne]/[complex **1a**] = 600. ^{e} Duration (h) = 0.17. ^{f} Duration (h) = 1. ^{g} Duration (h) = 4. ^{h} Duration (h) = 18.

Table 4. Cyclotrimerization of Alkynes to Benzene Derivatives Catalyzed by Complex 1b^{a} under Various Conditions in CH_2Cl_2 at Room Temperature

entry	R_1	R_2	product	yield (%)
25^{b,h}	H	Ph	**2**	99
26^{c,g}	H	Ph	**2**	96
27^{d,g}	H	Ph	**2**	46
28^{b,h}	*p*-tolyl	H	**3**	99
29^{c,g}	*p*-tolyl	H	**3**	93
30^{d,g}	*p*-tolyl	H	**3**	43
31^{b,h}	COOEt	COOEt	**5**	99
32^{c,g}	COOEt	COOEt	**5**	90
33^{d,g}	COOEt	COOEt	**5**	50
34^{b,h}	*n*-Bu	H	**7**	98
35^{c,g}	*n*-Bu	H	**7**	93
36^{d,g}	*n*-Bu	H	**7**	41
37^{b,h}	Et	Et	**9**	99
38^{c,g}	Et	Et	**9**	94
39^{d,g}	Et	Et	**9**	35
40^{b,h}	*n*-Pr	*n*-Pr	**10**	85
41^{c,g}	*n*-Pr	*n*-Pr	**10**	65
42^{d,g}	*n*-Pr	*n*-Pr	**10**	15

^{a} [complex **1b**] = 50 mg (0.085 mmol) in 20 mL of CH_2Cl_2. ^{b} [alkyne]/[complex **1b**] = 6. ^{c} [alkyne]/[complex **1b**] = 200. ^{d} [alkyne]/[complex **1b**] = 600. ^{e} Duration (h) = 0.17. ^{f} Duration (h) = 1. ^{g} Duration (h) = 4. ^{h} Duration (h) = 18.

Scheme 3. Reactions of a Mononuclear Complex Formed by the Reaction of 1a with Alkyne



Furthermore, the addition of a large excess of THT to the solution of the mononuclear complex after the trimerization of alkyne had finished did not provide the initial dinuclear complex **1a**. Similar results have been observed for reactions where **2a** was applied instead of **1a**. All those results suggest that this mononuclear complex is not a significant catalyst species in the catalytic trimerization of alkyne. **11** and **12** are formed by the degradation of a dinuclear complex with two 1,4-η^2-butadienes such as $[Nb_2(\mu\text{-}Cl)_2Cl_4(\eta^2\text{-}RC{=}CR{-}RC{=}CR)_2]$ (R = Et, Pr), which is supposed to be one of main intermediates in the catalytic cycle.

Reaction of alkyne with η^2-butadiene to give a benzene derivative has been known for other mononuclear complexes. Takahashi et al. reported that $C_6Ph_4Pr_2$ was formed by the reaction of $[NiCp_2(\eta^2\text{-}PhC{=}CPh{-}PhC{=}CPh)_2]$ with 1 equiv of 4-octyne, although C_6Et_6 and $C_6Pr_2Et_4$ were obtained by the reaction of $[ZrCp_2(\eta^2\text{-}EtC{=}CEt{-}EtC{=}CEt)_2]$ with 1 equiv of 3-hexyne and 4-octyne, respectively, in the presence of $NiBr_2(PPh_3)_2$.[23] In both those cases the Ni^{II} center may play an important role, probably as a Lewis acid. The Zr^{II} center with d^2 electron configuration, however, is not an effective active center alone without a nickel species, and the combination with Ni^{II} is important for the accomplishment of the trimerization. We have no evidence why the present dinuclear Nb^{III} complexes with d^2 configuration for each center can accomplish the trimerization. Cooperation of two metal centers bound directly with a metal−metal bond makes both σ-acid and π-base activities possible.

Evidence from NMR Measurements. The reaction of 2-hexyne with 1/6 equiv of **1a** in $CDCl_3$ (0.4 mL) was monitored by ^1H NMR at room temperature. Two groups of signals were observed at δ 3.13 and 1.87 (THT) and at 2.09, 1.78, 1.49, and 0.98 (2-hexyne), which are assigned to a dinuclear Nb^V intermediate, $[\{NbCl_2(THT)[\eta^2\text{-}(n\text{-}Bu)C{=}CMe]\}_2(\mu\text{-}Cl)_2]$ (**15**). The reaction was also monitored by ^{93}Nb NMR. The resonance of **1a** at δ −494 ($W_{1/2}$ = 1400 Hz) shifted to δ −480 (vs Nb_2Cl_{10}, $W_{1/2}$ = 1110 Hz) after the addition of 2-hexyne. Since the chemical shifts of the Nb^V species are generally observed in the range δ −700 to +1300,[34,35] the resonance can be assigned to **15**. When additional THT was poured into the solution after the intermediate **15** had been generated, the signal was observed at δ −494, again indicating the recovery of **1a**. Accordingly **15** is found to exist in an equilibrium between the original complex **1a** in solution. On the other hand, when 2-hexyne and 0.5 equiv of **1a** were mixed, ^1H NMR signals assigned to cyclotrimer **7** and free THT were observed. These results suggest that the rate-determining step of the overall catalytic process is the insertion of the second alkyne into an alkyne-bound intermediate **15** to give the dinuclear complex with two 1,4-η^2-butadiene derivatives.

Overall Catalytic Cycle. A plausible mechanism of the cyclotrimerization is shown in Scheme 4. NMR observations suggest that the first oxidative addition of the alkyne takes place onto the vacant site of each Nb^{III}, after the bridging THT leaves from **1**. There is no indication about the insertion into the Nb−(μ-Cl), Nb−(η-Cl), or Nb−(η-S) bond, which is claimed in the "sequential insertion" mechanism.[36] The high lability of the

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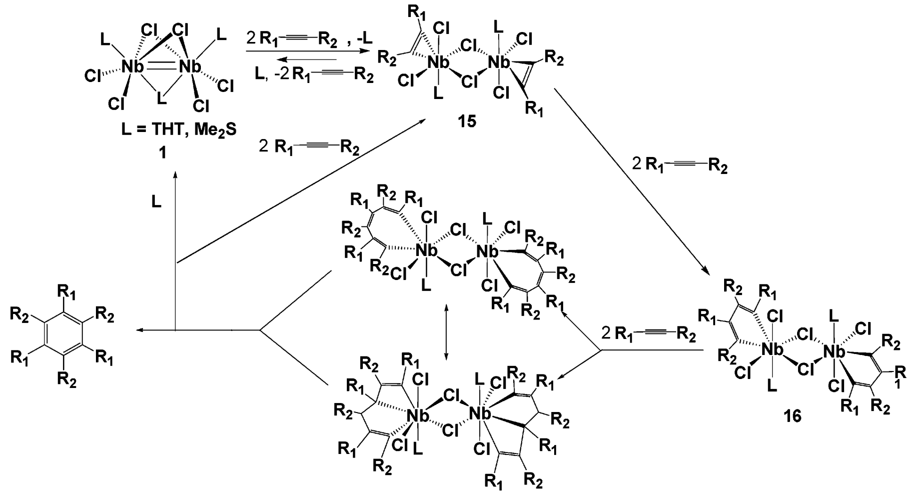
Scheme 4. Possible Cyclotrimerization Mechanism of Alkynes Catalyzed by Complex 1



bridging sulfur donor as a leaving group seems responsible for the reactivity. Through this process alkyne binds to Nb^V in the η^2 mode, giving a dinuclear intermediate **15**. This reaction is analogous to the formation of a dinuclear complex of congener tantalum(V), $[\{TaCl_2(THT)[\eta^2\text{-}(t\text{-}Bu)C{=}CMe]\}_2(\mu\text{-}Cl)_2]$, by the reaction of $[\{TaCl_2(THT)\}_2(\mu\text{-}Cl)_2(\mu\text{-}THT)]$ with $t\text{-}BuC{\equiv}CMe$.[5] This complex, however, does not give cyclotrimerized products. Probably this is because that the Ta complex is so inert in the insertion and addition of additional alkyne into the coordinated alkyne that the next and/or third steps are very slow.

In the present catalytic process, the 1,3,5-cyclotrimerized product was selectively available from various unsymmetrical alkynes. The second step, addition of the second alkyne to form a η^2-butadiene moiety, is the rate-determining and the key step for the regioselectivity. The carbon−carbon bond should be formed between incoming and coordinated alkynes, and this reaction should take place in the head-to-tail fashion. There are two possibilities for this process: first, the insertion of the second alkyne into the Nb−C bond; second, the addition of the second alkyne onto the C−C bond. If the reaction proceeds via the insertion, the electric factor seems to play an important role. Incoming alkynes with electron-donating substituents may tend to attach to the more positive Nb center than to the coordinated alkyne. On the other hand, incoming alkynes with the electron-withdrawing groups may bind to the more electron-donating carbon of the coordinated alkyne. On the other hand, if the direct addition is operative, both steric and electronic factors can affect the selectivity. The dinuclear structure is considered to play a significant role in this process, since catalysis of the mononuclear Nb and Ta complexes does not exhibit such regioselectivity.[17,18] An interesting example is $[TaCl_3(DME)(\eta^2\text{-}R_1C{=}CR_2)]$.[19] In the complex with 3-hexyne ($R_1 = t\text{-Bu}$, $R_2 = Me$) the bond length of one Ta−(alkyne-*C*) for the carbon located above the Cl−Ta−MeO plane (2.046 Å) is shorter than the other one, which is above the Cl−Ta−Cl plane (2.102 Å). On the other hand, in the complex with PhC═CMe, almost the same Ta−C bond lengths are observed: Ta−CPh above the Cl−Ta−MeO plane (2.053 Å) and Ta−CMe above the Cl−Ta−Cl plane (2.053 Å). Furthermore in the above-mentioned dinuclear Ta-η^2-alkyne complex $[\{Ta(\eta\text{-}Cl)_2(THT)[\eta^2\text{-}(t\text{-}Bu)C{=}CMe]\}_2(\mu\text{-}Cl)_2]$, the Ta−CMe bond above the THT−Ta−Cl plane is 2.029 Å and the Ta−CBu bond trans to the μ-Cl is 2.033 Å. These structural observations suggest, although rather indirectly, that the length and the strength of the metal−carbon bond are governed by both steric and electronic factors. In the present catalytic reaction, although the Nb-η^2-butadiene intermediate $[\{NbCl_2(THT)(\eta^2\text{-}R_1C{=}CR_2{-}R_1C{=}CR_2)\}_2(\mu\text{-}Cl)_2]$ (**16**) was not detected by NMR and FAB-MS measurements, the reactions of isolated mononuclear complexes, **11** and **12**, are not involved in the overall catalytic cycle, as evidenced from the reactions shown in Scheme 3. Therefore, the Nb-η^2-butadiene species **16** should be present even in a low concentration as an essential intermediate in the catalytic cycle. Therefore, although no direct evidence was available, the present catalytic reaction seems to be controlled by electronic factors influenced by the steric conditions in the coordination sphere.

Although it was an enormous effort to develop regio- and chemoselectivity in the formation of metallocyclopentadienylalkenyl intermediates, $M(\eta^2\text{-}R_1C{=}CR_2{-}R_3C{=}CR_4)(\eta^2\text{-}R_5C{=}CR_6)$, little success was achieved for the intermolecular [2+2+2] cycloaddition reaction.[37] Ladipo et al. have recently succeeded in preparing a titanium(IV) complex, $[Ti(DMSC)\{\eta^2\text{-}1,2,4\text{-}C_6H_3(SiMe_3)_3\}]$ (DMSC = 1,2-alternate Me_2Si-bridged *p-tert*-butylcalix[4]arene), and characterized it by spectroscopic methods and single-crystal X-ray techniques.[21] The regioselectivity in this cyclotrimerization reaction is not rigorously controlled by the electronic demand but by the steric factors of the calixarene cavity.

In the third step, the selective insertion of the third alkyne into the Nb−C bond may give the Nb-η^2-hexatriene complex, because Nb complexes with coordination numbers 7 and 8 are known to be general.[38] Accordingly, the formation of the metallocyclopentadienylalkenyl intermediate $[\{NbCl_2(THT)(\eta^2\text{-}R_1C{=}CR_2{-}R_1C{=}CR_2)(\eta^2\text{-}R_1C{=}CR_2)\}_2(\mu\text{-}Cl)_2]$ may be difficult. Furthermore, this process seems to be influenced by the electronic factors as the second step is. The reductive elimination process of the cyclotrimer proceeds presumably through a "common" mechanism[39] proposed by Schore or substitution of alkyne for the coordinated metallacyclotrimer. Thus, the mechanism in Scheme 4 is suggested, although none of the dinuclear niobapentadiene or niobaheptatriene intermediates have been detected by reactions of complex **1a** or **1b** with unsymmetrical alkynes.

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[37] For regioselective stoichiometric reactions of $M(\eta^2\text{-}R_1C{=}CR_2{-}R_3C{=}CR_4)(\eta^2\text{-}R_5C{=}CR_6)$ with diphenylacetylene, see: (M = Co) (a) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549. (M = Pd) (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

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3. Conclusion

The structure of **1a** was determined by X-ray crystallography to be a dinuclear structure with a $Nb^{III}-Nb^{III}$ double bond with a distance of 2.6912(4) Å. The reaction of **1a** with Me_2S did not give **1b**, while the reaction of **1b** with THT leads to **1a**. The regioselective head-to-tail cyclotrimerization of various alkynes took place in the presence of $[\{NbCl_2L\}_2(\mu\text{-}Cl)_2(\mu\text{-}L)]$ (L = THT, Me_2S, **1**) commonly to give 1,3,5-(X_3)-2,4,6-(Y_3)-hexasubstituted benzene derivatives (**2**−**10**) in high yields. The dinuclear structure of the complexes may be responsible for the novel regioselectivity. The stronger the electron-withdrawing ability of the substituents on the alkyne, the higher the yield of the cyclotrimerized product.

4. Experimental Section

All the reactions were carried out under an atmosphere of dry argon by using standard Schlenk tube techniques. All the solvents were dehydrated and purified by distillation: Et_2O was refluxed over $LiAlH_4$ and distilled; CH_2Cl_2, toluene, and *n*-hexane were refluxed over CaH_2 and distilled. These purified solvents were stored under an argon atmosphere. Other reagents employed in the research were of reagent grade and used as received without further purification.

IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. ^1H and ^{13}C NMR spectra (400 MHz for ^1H, 100.6 MHz for ^{13}C NMR) were recorded on a Bruker DRX-400 or a Bruker AM-400 NMR spectrometer. ^{93}Nb NMR spectra (97.9 MHz for ^{93}Nb) were recorded on a Bruker AM-400 NMR spectrometer. The reference was as follows: for ^1H and ^{13}C NMR, Me_4Si as an internal standard ($\delta = 0$); for ^{93}Nb NMR, Nb_2Cl_{10} in CD_3CN as an external standard ($\delta = 0$). FAB-MS spectra were recorded on a JEOL JMS-700AM mass spectrometer. Elemental analyses were carried out using a FISONS EA 1108 analyzer at the Material and Life Science Research Center of Saitama University.

Crystals of **1a** were grown in CH_2Cl_2−hexane (C_6H_{12}) at room temperature and submitted for X-ray crystallography measurements. Data were collected on a Bruker SMART APEX CCD area-detector diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The structures were solved by a direct method using SHELXTL-NT software and refined by the full-matrix least-squares method in the SHELXTL-NT system. The final refinement with anisotropic thermal parameters converged to $R = 0.0456$ and $R_w = 0.0906$ for 2851 independent reflections with $F_o > 2\sigma(F_o)$.

Preparation of $[\{NbCl_2(THT)\}_2(\mu\text{-}Cl)_2(\mu\text{-}THT)]$ (1a). A mixture of diniobium decachloride (Nb_2Cl_{10}, 2.3 g, 4.3 mmol), tetrahydrothiophene (C_4H_8S, THT, 2.0 mL, 23.4 mmol), and magnesium (Mg, 0.57 g, 23.4 mmol) was dissolved in a mixture of dichloromethane (CH_2Cl_2, 75 mL) and diethyl ether (Et_2O, 11.5 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The solution caused the formation of a precipitate, which was removed by suction filtration. The resultant filtrate was concentrated to dryness, leaving a purple powder. The crude product was washed with hexane and dried under reduced pressure. The complex **1a** thus obtained was recrystallized from CH_2Cl_2−hexane to give purple crystals (2.4 g, yield 86%). ^1H NMR ($CDCl_3$, 300 K): δ 4.03 (4H, H_α, bridge-C_4H_8S), 3.41 (8H, H_α, terminal-C_4H_8S), 2.31 (4H, H_β, bridge- C_4H_8S), 2.15 (8H, H_β, terminal-C_4H_8S). $^{13}C\{^1H\}$ NMR (300 K, $CDCl_3$): δ 38.0 (2C, C_α, bridge-C_4H_8S), 35.7 (4C, C_α, terminal-C_4H_8S), 30.4 (4C, C_β, terminal-C_4H_8S), 27.9 (2C, C_β, bridge-C_4H_8S). ^{93}Nb NMR (300 K, $CDCl_3$): δ −494 ($W_{1/2} = 1400$ Hz). Anal. Found (calcd for $C_{12}H_{24}Cl_6S_3Nb_2$): C, 21.61 (21.74); H, 3.53 (3.65). UV−vis (CH_2Cl_2): λ_{max}, 536 nm ($\epsilon_{max} = 92\,000$ M^{-1} cm^{-1}). FAB-MS/DMSO: 664 (M^+ 100%).

Preparation of $[\{NbCl_2(Me_2S)\}_2(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)]$ (1b). The complex was prepared by the method proposed in the literature.[3f] A mixture of Nb_2Cl_{10} (2.3 g, 4.3 mmol), dimethyl sulfide (C_2H_6S, SMe_2, 1.71 mL, 23.4 mmol), and Mg (0.57 g, 23.4 mmol) was dissolved in a mixture of CH_2Cl_2 (75 mL) and Et_2O (11.5 mL) at room temperature. The mixture was stirred for 2 days at room temperature. The solution caused the formation of a precipitate, which was removed by suction filtration. The resultant filtrate was concentrated to dryness, leaving a purple powder. The crude product was washed with hexane and dried under reduced pressure. The complex **1b** thus obtained was recrystallized from CH_2Cl_2−hexane to give purple crystals (2.2 g, yield 88%). ^1H NMR ($CDCl_3$, 300 K): δ 3.33 (6H, bridge-Me_2S), 2.63 (12H, terminal-Me_2S). $^{13}C\{^1H\}$ NMR (300 K, $CDCl_3$): δ 30.0 (2C, bridge-Me_2S), 22.7 (4C, terminal-Me_2S). ^{93}Nb NMR (300 K, $CDCl_3$): δ −495 ($W_{1/2} = 1320$ Hz). Anal. Found (calcd for $C_{12}H_{24}Cl_6S_3Nb_2$): C, 12.38 (12.32); H, 3.10 (2.93).

Reaction of 1b and THT. THT (0.05 mL, 0.56 mmol) was added to **1b** (100 mg, 0.17 mmol) in CH_2Cl_2 (20 mL) and stirred for 2 days at room temperature. The solution caused the formation of a precipitate, which was removed by suction filtration. The resultant filtrate was concentrated to dryness, leaving purple powders. The crude product was washed with hexane and dried under reduced pressure. **1b** could be obtained as a purple powder (90 mg, yield 80%). This complex was identified by ^1H and $^{13}C\{^1H\}$ NMR spectra.

Catalytic Cyclotrimerization of Alkynes with 1. General Procedure. Alkyne (0.45 or 15 or 45 mmol) was added to complex **1a** (50 mg, 0.075 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred at room temperature. The solution caused the formation of a precipitate, which was removed by suction filtration. The resultant filtrate was concentrated to dryness. The crude product was washed with hexane and dried under reduced pressure. The same procedures were applied to **1b** (50 mg, 0.085 mmol) in CH_2Cl_2 (20 mL) with alkyne (0.45, 15, or 45 mmol). The results are collected in Tables 3 and 4, respectively.

Analysis Data. Compound **2**: ^1H NMR ($CDCl_3$, 300 K) δ 7.79 (s, 3H, C_6H_3, 1,3,5-$(C_6H_5)_3C_6H_3$), 7.70 (d, $J = 7.0$ Hz, 6H, *o*-C_6H_5, 1,3,5-$(C_6H_5)_3C_6H_3$), 7.47 (t, $J = 5.4$ Hz, 3H, *m*-C_6H_5, 1,3,5-$(C_6H_5)_3C_6H_3$), 7.38 (tt, $J = 7.5$, 1.6 Hz, 6H, *p*-C_6H_5, 1,3,5-$(C_6H_5)_3C_6H_3$). Compound **3**: ^1H NMR ($CDCl_3$, 300 K) δ 7.72 (s, 3H, C_6H_3, 1,3,5-$(C_6H_4\text{-}p\text{-}CH_3)_3C_6H_3$), 7.58 (d, $J = 8.0$ Hz 6H, *o*-C_6H_4-*p*-CH_3, 1,3,5-$(C_6H_4\text{-}p\text{-}CH_3)_3C_6H_3$), 7.28 (d, $J = 8.0$ Hz, 6H, *m*-C_6H_4-*p*-CH_3, 1,3,5-$(C_6H_4\text{-}p\text{-}CH_3)_3C_6H_3$), 2.41(s, 9H, 1,3,5-$(C_6H_4\text{-}p\text{-}CH_3)_3C_6H_3$, 1,3,5-$(C_6H_4\text{-}p\text{-}CH_3)_3C_6H_3$). Compound **4**: ^1H NMR ($CDCl_3$, 300 K) δ 3.39 (12H, $-CH_2$, $C_6(CH_2)_6$); mp 287.5 °C. Compound **5**: ^1H NMR ($CDCl_3$, 300 K) δ 4.45−4.05 (br, 12H, $-COOCH_2CH_3$, $C_6(COOCH_2CH_3)_6$), 1.50−1.20 (br, 18H, $-COOCH_2CH_3$, $C_6(COOCH_2CH_3)_6$); mp 38 °C. Compound **6**: ^1H NMR ($CDCl_3$, 300 K) δ 2.63 (m, 2H, CH_2, $CH_3CH_2CH_2$), 1.22 (m, 2H, CH_2, $CH_3CH_2CH_2$), 1.18 (m, 2H, CH_3, $CH_3CH_2CH_2$), 1.01 (m, 2H, CH_3, CH_3). Compound **7**: ^1H NMR ($CDCl_3$, 300 K) δ 6.80 (s, 3H, C_6H_3, 1,3,5-$(CH_3CH_2CH_2CH_2)_3C_6H_3$), 2.54 (t, $J = 8.0$ Hz, 2H, $CH_3CH_2CH_2CH_2$, 1,3,5-$(CH_3CH_2CH_2CH_2)_3C_6H_3$), 1.58 (m, 2H, $CH_3CH_2CH_2CH_2$, 1,3,5-$(CH_3CH_2CH_2CH_2)_3C_6H_3$), 1.37 (m, 2H, $CH_3CH_2CH_2CH_2$, 1,3,5-$(CH_3CH_2CH_2CH_2)_3C_6H_3$), 0.94 (t, $J = 7.5$ Hz, 3H, $CH_3CH_2CH_2CH_2$, 1,3,5-$(CH_3CH_2CH_2CH_2)_3C_6H_3$). Compound **8**: ^1H NMR ($CDCl_3$, 300 K) δ 7.61 (s, 3H, C_6H_3, $C_6H_3(Me_3Si)_3$), 0.20 (s, 27H, Me_3Si, $C_6H_3(Me_3Si)_3$).

Reaction of 1a with 6 equiv of 3-Hexyne and 4-Octyne. General Procedure. 3-Hexyne (0.45 mmol) was added to **1a** (50 mg, 0.075 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 18 h at room temperature. The resulting precipitates were removed by filtration. The resultant filtrate was concentrated to dryness. The crude product was washed with hexane and dried under reduced pressure. Complex **11** thus obtained was recrystallized from CH_2Cl_2−hexane to give blue crystals (14 mg, yield 26%). Cyclotrimer **9** was obtained by the drying of the washings of crude **11** as a pale yellow solid (22 mg, 60%). The same procedures were applied to 4-octyne (0.45 mmol) to obtain complex **12** (recrystallized from CH_2Cl_2−hexane, blue crystals, 37 mg, 58%) and cyclotrimer **10** (white solid, 19 mg, 40%).

Analysis Data. Compound **9**: ^1H NMR ($CDCl_3$, 300 K) δ 2.63 (q, $J = 7.0$ Hz, 12H, $CH_3C\mathit{H}_2$, $C_6(CH_3C\mathit{H}_2)_6$, 1.19 (tt, $J = 18.7$, 7.5 Hz, 18H, $C\mathit{H}_3CH_2$, $C_6(C\mathit{H}_3CH_2)_6$); FAB-MS/NBA 247 (M^+ 100%). Compound **10**: ^1H NMR ($CDCl_3$, 300 K) δ 2.40−2.50 (m, 12H, $CH_3CH_2C\mathit{H}_2$, $C_6(CH_3CH_2C\mathit{H}_2)_6$), 1.50−1.60 (m, 12H, $CH_3C\mathit{H}_2CH_2$, $C_6(CH_3C\mathit{H}_2CH_2)_6$), 1.04 (t, $J = 7.0$, 18H, $C\mathit{H}_3CH_2CH_2$, $C_6(C\mathit{H}_3CH_2CH_2)_6$). Complex **11**: ^1H NMR ($CDCl_3$, 300 K) δ 3.3−3.1 (m, 8H, $CH_3C\mathit{H}_2$, $NbCl_3C_4(CH_3C\mathit{H}_2)_4$, 1.05−0.95 (m, 12H, $C\mathit{H}_3CH_2$, $NbCl_3C_4(C\mathit{H}_3CH_2)_4$); FAB-MS/NBA 364 ($M^+$ 100%). Complex **12**: ^1H NMR ($CDCl_3$, 300 K) δ 3.00−3.30 (m, 8H, $CH_3CH_2C\mathit{H}_2$, $C_6(CH_3CH_2C\mathit{H}_2)_6$), 1.25−1.45 (m, 8H, $CH_3C\mathit{H}_2CH_2$, $C_6(CH_3C\mathit{H}_2CH_2)_6$), 0.7−0.9 (m, 12H, $C\mathit{H}_3CH_2CH_2$, $C_6(C\mathit{H}_3CH_2CH_2)_6$).

Reaction of 1a with 200 or 600 equiv of 3-Hexyne or 4-Octyne. To **1a** (50 mg, 0.075 mmol) in CH_2Cl_2 (20 mL) was added 3-hexyne (15 or 45 mmol) or 4-octyne (15 or 45 mmol), and the mixture was stirred for 1 h at room temperature. Precipitates were removed by filtration, and the filtrate was concentrated to dryness under reduced pressure.

Reactions of 11 and 12 with 1 equiv of 3-Hexyne and 4-Octyne. To **11** (50 mg, 0.14 mmol) in CH_2Cl_2 (20 mL) was added 3-hexyne (0.015 mL, 0.14 mmol) or 4-octyne (0.020 mL, 0.14 mmol), and the mixture was stirred for 18 h at room temperature, filtered, and concentrated to dryness. The crude product was washed with hexane and dried under reduced pressure. Cyclotrimer **9** thus obtained from 3-hexyne was recrystallized from CH_2Cl_2−hexane to give colorless crystals (33 mg, yield 98%). Cyclotrimer **13** from 4-octyne was a white powder (23 mg, 61%). The same procedures were applied to the reaction of **12** (50 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) with 3-hexyne (0.014 mL, 0.12 mmol) or 4-octyne (0.018 mL, 0.12 mmol). Cyclotrimer **10** from 4-octyne was recrystallized from CH_2Cl_2−hexane to give colorless crystals (31 mg, 80%). Cyclotrimer **14** from 3-hexyne was a white powder (23 mg, 65%).

Analyisis Data. Compound **13**: ^1H NMR ($CDCl_3$, 300 K) δ 2.63 (q, $J = 7.0$ Hz, 4H, $CH_3C\mathit{H}_2$, $C_6(CH_3CH_2CH_2)_2(CH_3C\mathit{H}_2)_4$), 2.61 (q, $J = 7.1$ Hz, 4H, $CH_3C\mathit{H}_2$, $C_6(CH_3CH_2CH_2)_2(CH_3C\mathit{H}_2)_4$), 2.43−2.55 (m, 4H, $CH_3CH_2C\mathit{H}_2$, $C_6(CH_3CH_2C\mathit{H}_2)_2(CH_3CH_2)_4$), 1.52−1.58 (m, 4H, $CH_3C\mathit{H}_2CH_2$, $C_6(CH_3C\mathit{H}_2CH_2)_2(CH_3CH_2)_4$), 1.19 (t, $J = 7.3$ Hz, 12H, $C\mathit{H}_3CH_2$, $C_6(C\mathit{H}_3CH_2CH_2)_2(CH_3CH_2)_4$), 1.05 (t, $J = 7.2$ Hz, 6H, $C\mathit{H}_3CH_2CH_2$, $C_6(C\mathit{H}_3CH_2CH_2)_2(CH_3CH_2)_4$). Compound **14**: ^1H NMR ($CDCl_3$, 300 K) δ 2.55−2.70 (m, 4H, $CH_3C\mathit{H}_2$, $C_6(CH_3CH_2CH_2)_4(CH_3C\mathit{H}_2)_2$), 2.30−2.55 (m, 8H, $CH_3CH_2C\mathit{H}_2$, $C_6(CH_3CH_2C\mathit{H}_2)_4(CH_3CH_2)_2$), 1.45−1.75 (m, 8H, $CH_3C\mathit{H}_2CH_2$, $C_6(CH_3C\mathit{H}_2CH_2)_4(CH_3CH_2)_2$), 1.18 (t, $J = 8.1$ Hz, 6H, $C\mathit{H}_3CH_2$, $C_6(CH_3CH_2CH_2)_4(C\mathit{H}_3CH_2)_2$), 1.01 (t, $J = 7.7$ Hz, 12H, $C\mathit{H}_3CH_2CH_2$, $C_6(C\mathit{H}_3CH_2CH_2)_4(CH_3CH_2)_2$).

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Areas Metal-Assembled Complexes (No. 10149208) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: X-ray crystallographic files in CIF format for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0601100